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CORRELATION BETWEEN THE SIZE DISTRIBUTION OF BUBBLES AND SOLID PARTICLES IN THE PROCESS OF FORMATION OF AGGREGATES FROM THEM

Z. V. Volkova

In 1937 we established, on the basis of a study of the adhesion mechanism of air bubbles to very small and uneven surfaces of solid particles [1], that aggregates of two types may be formed from air bubbles and particles: 1) mineralized bubbles, in which the area of adhesion is mainly determined by the size of the particles, and 2), the floccules, the formation of which is based on aggregates of sufficiently large particles and small bubbles attached to parts of their surface. As the size of the particles increases in the formation of aggregates of the first type, the volume of the bubbles mineralized by them should increase.

Further study of the relationship between the dimensions of the bubbles and of the particles led to the conclusion [1] that sufficiently small particles, the dimensions of which depend on the density, form aggregates of a third type, mineralized bubbles, the surface of which is covered by a continuous "crust" of particles. Microphotographs of foam [1], obtained from fractionated powders, confirmed: 1) the formation of aggregates of the types described from air bubbles and solid particles, and 2) the dependence of the volume of the mineralized bubbles on the dimensions of the particles. Aleinikov's studies [2] confirmed the formation of aggregates of the above three types from air bubbles and particles of coal.

The results of our studies during 1945-1948 [3, 4] on the interdependence of the particles' size $\underline{b}$, the bubble volume $\underline{V}$ and the adhesion angle α*, may be summarized by the following systems of curves for the dependence of α on $\underline{b}$, when $\underline{V}$ = const. (Figure 1), and of α on $\underline{V}$ when $\underline{b}$ = const. (Figure 2). These systems of curves indicate an analogy between the influence of the bubble volume and of the particle size on the type of aggregates formed from them. For each particle there exists a certain range of volumes of bubbles which adhere to it $[\underline{V}_k - \underline{V}_m]$, and for each bubble, there is a range of sizes $[\underline{b}_k - \underline{b}_m]$ of adhering particles in the process of formation of aggregates of the first type.

The ranges of bubble volumes $[\underline{V}_k - \underline{V}_m]$ and particle sizes $[\underline{b}_k - \underline{b}_m]$ increase with increasing angle of adhesion, that is, with decrease of the wettability of the particle surfaces. Figure 3 shows curves for $[\underline{b}, \underline{V}_k]$ and $[\underline{b}, \underline{V}_m]$ for the values of 30° and 40° for the limiting angles of adhesion α_k. Intersections with the straight lines for $\underline{b}$ = const. gives the volume range $[\underline{V}_k - \underline{V}_m]$ for bubbles which adhere to a particle of the given dimensions; intersections with the straight lines for $\underline{V}$ = const. determine the range of particle sizes which adhere to a bubble of the given volume.

It might be thought that aggregates of the first type are formed from bubbles and particles the size range of which is limited by the curves $[\underline{b}, \underline{V}_m]$ and $[\underline{b}, \underline{V}_k]$; bubbles of volume less than $\underline{V}_m$ can adhere to regions on the surface of particles smaller than them in size. However, the volumes of the minimal bubbles $\underline{V}_m$ are very small, especially for large angles of adhesion. A bubble of volume $\underline{V}_m$ cannot ensure the ascent of a particle of sufficiently high density.

It seems to us more correct to calculate the minimum volume of bubbles forming aggregates of the first type from the impulse which ensures the ascent of at least two particles, by means of the Formula:

$$\underline{V}_m = \frac{4b^3(\rho - \rho_1)}{[\rho_1 - \rho_0]} \qquad (1)$$

where ρ, ρ_1, and ρ_0 are the densities of the particles, water, and air, respectively.

Figure 3 shows a curve for the dependence of values of $\underline{V}_m$ on particle size $\underline{b}$ for $\rho = 4 \text{g/cm}^3$. Below this curve, aggregates of the second type are formed for all dimensions of particles and bubbles; ascent of the particles can be ensured by several bubbles.

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* Here $\alpha = \theta - \gamma$, where θ is the angle of wetting of the solid and γ is the angle of the shape of the particle surface.

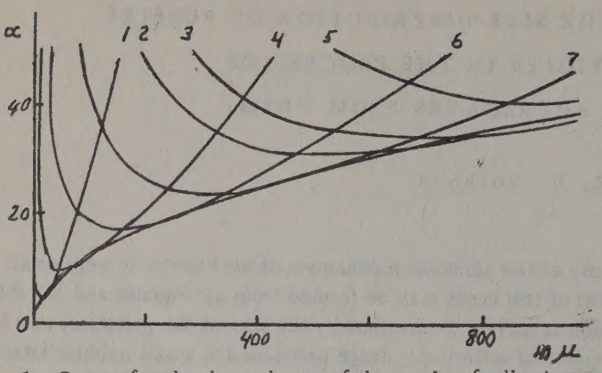

Fig. 1. Curves for the dependence of the angle of adhesion on particle size, for bubbles of the volume: 1) $0.523 \cdot 10^{-6}$; 2) $3.05 \cdot 10^{-3}$; 3) $5.57 \cdot 10^{-3}$; 4) $3.35 \cdot 10^{-5}$; 5) $9.16 \cdot 10^{-3}$; 6) $1.13 \cdot 10^{-4}$; 7) $5.23 \cdot 10^{-4}$.

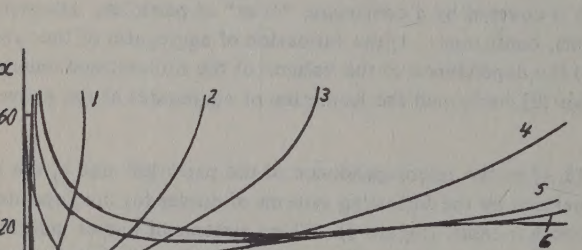

Fig. 2. Curves for the dependence of the angle of adhesion α on bubble volume for particles of the size: 1) 50; 2) 150; 3) 250; 4) 500; 5) 800; 6) 1000 μ.

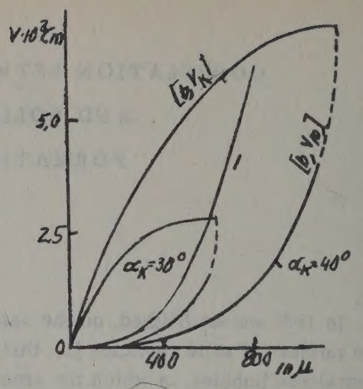

Fig. 3. Curves for the dependence of the maximum and minimum bubble volume on the particle size for α_k = 40 and 30°; 1 - curve for the dependence of the minimum bubble volume on the particle size (calculated from the impulse for the ascent of two particles).

On the basis of laws for the formation of aggregates of the first type, we proposed [1, 3] a statistical theory for the foam flotation process for the separation of solids. For given physical conditions for this process (content of the substance separated, distribution of particles by size and bubbles by volume, surface and other properties of the solids), methods were developed for calculating: 1) the probability of mineralization of each bubble; 2) the coefficient for the transfer of the substance separated to foam; 3) the kinetics of this process; 4) the probable factors for the distribution of powders with different surface characteristics, etc. On the basis of the statistical theory of the foam flotation process we concluded that there must be a statistical correspondence between the distribution of bubbles and particles, for optimum conditions of separation of solids, maximum separation coefficient, and high kinetics and quality factors in the process. The necessity for a correct selection of foam formers and the highest degree of dispersion of air in order to attain high kinetics and quality factors in the form flotation process provides a practical basis for the desirability of approaching statistical correspondence between the distributions of bubbles and particles in the process.

Earlier [3, 4] we examined the formation of aggregates from air bubbles and particles under conditions of statistical correspondence and with deviations from it by displacement of the particle distribution in the direction of larger sizes. In such conditions the formation of aggregates not only of the first but also of the second type becomes probable.

Calculations of the process of formation of aggregates of the first and second type, and their transfer to foam, may be made taking into account the distribution of all the bubble and particle fractions between aggregates of the first and second type.

Let the particle size distribution function for the solid separated be $\underline{F}_b(b)$, and bubble volume function be $\underline{F}_V(V)$. The content $\Delta \underline{W}_i$ of particles of the fraction $\underline{b}_i$, $\underline{b}_i + \underline{db}$, from which mineralized bubbles can be formed is determined by the fraction of the volume of the bubbles which adhere to them in the formation of aggregates of the first type, when

$$\Delta W_{i1} = \varphi_1(b_i)db = F_b(b_i)db \frac{\int\limits_{V_{mi}}^{V_{ki}} VF_V(V)\,dV}{\int\limits_{0}^{V_k} VF_V(V)dV} \tag{2}$$

where $(V_{ki} - V_{mi})$ is the range of bubble dimensions in these aggregates.

The content of particles of the fraction b_i, $b_i + db$ from which aggregates of the second type are formed is in this case:

$$\Delta W_{i2} = \varphi_2(b_i)db = F_b(b_i)db \frac{\int\limits_{0}^{V_{mi}} VF_V\ (V)dV}{\int\limits_{0}^{V_k} VF_V\ (V)dV} \tag{3}$$

From each fraction of bubble volumes Vj, $Vj + dV$ aggregates of the first and second types are formed. The content ΔW_{j1} of bubbles in this fraction, from which aggregates of the first type are formed, may be calculated from the Formula:

$$\Delta W_{j1} = \psi_1(V_j\ dV = F_V(V_j)dV \frac{\int\limits_{b_{mj}}^{b_{kj}} b^3F_b(b)db}{\int\limits_{0}^{b_k} b^3F_b(b)\,db} \tag{4}$$

where $[b_{kj} - b_{mj}]$ is the range of particle sizes which adhere to a bubble of volume V_j during formation of aggregates of the first type. Formation of aggregates of the second type takes place from bubbles of the fraction V_j, $V_j + dV$ with the content:

$$\Delta W_{j2} = \psi_2(V_j)dV = F_V\,(V_j)\,dV \frac{\int\limits_{b_{kj}}^{b_k} b^3F_b\,(b)\,db}{\int\limits_{0}^{b_k} b^3F_b\,(b)\,db} \tag{5}$$

In our previous papers, the calculation of transfer of solid particles into the foam was calculated for fairly disperse powders, from which aggregates of the first type only could be formed in the presence of a statistical correspondence between the distributions of bubbles and particles, or with a distribution determined by a curve displaced in the direction of larger volumes relative to statistical correspondence. The probability of mineralization of a bubble was assumed to be proportional to the content of particle adhering to it in the size range $[b_k - b_m]$.

For a more coarsely disperse powder with its great diversity of particle size, it is more reliable to calculate the probability of mineralization of each bubble from the volume yield of particles in the size range $[b_k - b_m]$. The probability of mineralization of a bubble is then proportional not to the content of the particles of the substance separated, but to their volume yield in the mixture of powders, which coincides with the particle content only if the distribution of the components of the mixture of powders is equal.

To calculate the probability of mineralization of an air bubble of radius R_i which ascends with the velocity u_i to meet particles falling with velocity u_p, for a volume content of the powder separated c, volume of water V_e, and volume of air V_g* we proposed the following Formula for 1 g of powder in a pulp:

$$\eta_{Vi} = c\frac{\pi R_i^2(u_i + u_p)}{V_e + V_g + \frac{1}{\rho}} \sin^2\beta \frac{\int\limits_{b_{mi}}^{b_{ki}} b^3\varphi_1(b)db}{\int\limits_{0}^{b_k} b^3F_b\,(b)\,db} \tag{6}$$

---

* Under conditions of dynamic equilibrium of the process of formation and evolution of bubbles, their content in the pulp, V_g cm^3/g and their volume distribution remain constant.

where $\bar{\rho}$ is the average density of the powders in the pulp; β is the angle of attachment of the particles by the bubble, which depends on the time of formation of three-phase boundaries during the adhesion of the particles of the separated substance to the bubble.

The coefficient of transfer of particles of the separated substance during formation of aggregates of the first type, η_V, may be calculated from the probability of mineralization of each bubble, η_{Vi}, and the distribution function for the bubble from which aggregates of the first type are formed

$$\eta_{Vi} = V_g \frac{\int_0^{V_k} \eta_{Vi}(V)\, \Psi_1(V)\, dV}{\int_0^{V_k} V F_V(V)\, dV} \tag{7}$$

The coefficient of transfer to foam of aggregates of the second type may be calculated from the transfer coefficient of the bubbles which adhere to the large particles, which is proportional to it. It is supposed that the adhesion of bubbles ascending with velocity u_i toward a particle falling with velocity u_p is effected in the same way as the adhesion of particles to a bubble, examined previously. If the particle has a rounded shape and its angle of attachment to the bubbles is the same as in the formation of aggregates of the first type, β, then the probability of the formation of an aggregate of the second type for a particle with the dimensions b_j is:

$$\eta_{bj} = V_g \frac{\pi b_j^2 (u_p + u_i)}{4\left(V_e + V_g + \frac{1}{\bar{\rho}}\right)} \sin^2\beta \frac{\int_0^{V_{mi}} V \Psi_2(V)\, dV}{\int_0^{V_k} V F_V(V)\, dV} \tag{8}$$

The transfer coefficient for air bubbles, and consequently also for the particles in the formation of aggregates of the second type may then be calculated from the Formula:

$$\eta_b = \frac{c}{2} \frac{\int_0^{b_k} \eta_{b_j}(b)\, \varphi_2(b)\, db}{\int_0^{b_k} b^3 F_b(b)\, db} \tag{9}$$

The average volume of a bubble which adheres to a particle of size b_j during formation of aggregates of the second type is

$$\bar{V}_j = \frac{\int_0^{V_{mj}} V \Psi_2(V)\, dV}{\int_0^{V_{mj}} \Psi_2(V)\, dV} \tag{10}$$

If the whole surface of a particle of size b_j is covered with bubbles of volume V_j, then it can receive the impulse necessary for ascent, under the condition

$$b_j < \frac{2\rho}{[\rho - \rho_1]} \sqrt[3]{\frac{6V_j}{\pi}} \tag{11}$$

In the calculation of the coefficient of transfer to foam of aggregates of the second type [see Equation (9)] it appears to be correct to calculate the upper limit of the dimensions of the floating particles b_k from Equation (11), and not from the maximum dimensions of the particles of the powder being floated.

The transfer of particles of the separated substance during the formation of aggregates of the first and second types is equal to

$$\eta = \eta_V + \eta_b. \tag{12}$$

The dependence on time of the degree of extraction m/m$_0$ of the substance into the foam may be calculated from the equation previously derived by us [1]:

$$[1-c]\frac{m/m_0}{[1-m/m_0]}+c\ln\frac{1}{[1-m/m_0]}=\eta t \tag{13}$$

The effect of displacement of the distribution curve for the particles in the direction of greater sizes, or of the distribution curve for the bubbles in the direction of smaller volumes, resulting in deviations from statistical correspondence of the distributions of bubbles and particles, on the separation process, may be observed by a specimen calculation for the separation of barytes powder into foam. Let us assume that the limiting angle of adhesion of air to the surface of barytes $\alpha_k = 40°$, its volume content in a mixture with quartz $c = 0.11$; the distribution curves calculated for the volume content of the fraction of barytes powder X_b have the appearance shown in Figure 4: Curve I for powder with particle sizes from 0 to 0.180 mm, Curve II for a powder with the same distribution, but with particle sizes from 0 to 0.720 mm.

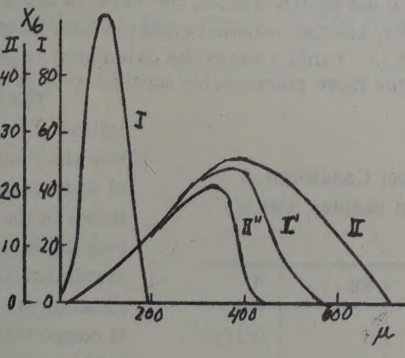

Fig. 4. Distribution curves for barytes powder (explanation in text).

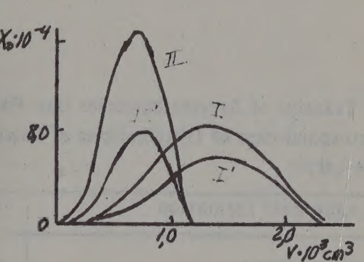

Fig. 5. Distribution curves for bubbles (explanation in text).

Figure 5 shows curves for the distribution of bubbles by volume: Curve I corresponds statistically to the distribution of particles from 0 to 0.180 mm in size (Curve I, Figure 4); in Curve II of this Figure the range of bubble volumes is halved in comparison with Curve I.

From the values of ΔW_{i1}, ΔW_{i2}, ΔW_{j1} and ΔW_{j2}, calculated from Formulas (2-5), the volume content of the particles X_b and of the bubbles X_V of all the fractions was distributed between aggregates of the first and second types for the following three processes of separation of barytes particles into foam:

1. Barytes powder with particles from 0 to 0.180 mm in size (Curve I, Figure 4) is separated out by bubbles having a statistically equivalent volume distribution (Curve I, Figure 5).

2. Barytes powder with distribution according to Curve II Figure 4 (with particles up to 0.720 mm in size) is separated out by bubbles with the same distribution as in the previous case.

3. The same coarsely dispersed powder with particles from 0 to 0.720 mm is separated out by bubbles with a distribution according to Curve II, Figure 5, (the range of bubble volumes is from 0 to $1.2 \cdot 10^{-3}$ cm^3).

Transition from Curve I to II of Figure 5 corresponds to a change of maximum bubble diameter from 1.6 to 1.33 mm.

In the first of the three processes for the separation of barytes only aggregates of the first type are formed. On the basis of a calculation of the distribution of the volume content of all the fractions of barytes powder particles and of the bubbles between aggregates of the first and second types in the second process, Curve II' (Figure 4) for distribution of particles, and Curve I' (Figure 5) for the distribution of bubbles, from which aggregates of the second type are formed, were plotted. In the third process aggregates of the first type are formed from particles with a size distribution given by Curve II" (Figure 4), and bubbles with a distribution given by the Curve II' (Figure 5). Aggregates of the second type are formed from the bubbles and particles of all fractions, the distribution of which is included between Curves II and II" (Figure 4) and II and II' (Figure 5).

Displacement of the distribution curve for the particles in the direction of larger dimensions, and for the bubbles in the direction of smaller volumes leads to an increase of the volume content of large particles and small bubbles, from which aggregates of the second type are formed. In the second process aggregates of the first type are formed from 65%, and in the third process from 45% of the volume of all the bubbles and particles.

Formulas (7-10) were used to calculate the probabilities η_{Vi} of mineralization of the bubbles of each fraction, η_{bi} of covering the large particles by small bubbles, and the coefficients of transfer to foam, η_V and η_b. For 1g of the powder mixture, the value V_e for the volume of water in the pulp was taken as 4 cm^3 and that of the air V_g as 1 cm^3. As in our earlier studies, the value of $\sin^2\beta$ was taken as 0.171, and the volume content of barytes in the mixture as 0.11. Table 1 shows the calculated values of η_V, η_b and η for the three processes for separation of barytes into foam.

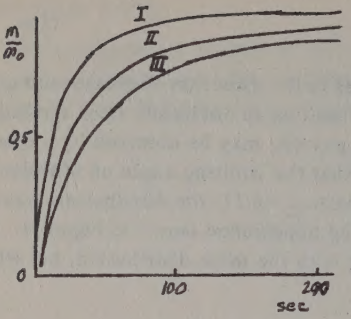

Fig. 6. Curves showing the dependence of degree of extraction on time (explanation in text).

The probability of separation of barytes powder into the foam during formation of aggregates of the second type, shown in the table, may decrease considerably in practice, as the maximum dimensions of an ascending particle when its surface is completely covered by air bubbles [see equation (11)], which are 0.913 mm in the second process and 0.725 mm in the third, are very close to the dimensions of the large particles of barytes of distribution curve II (Figure 4).

TABLE 1

Probability of Transfer of Barytes Particles into Foam, under Conditions of Statistical Correspondence of Distributions of Particles and Bubbles, and in Absence of ~~the Latter~~

Conditions of aggregate formation	η_V	η_b	η
Statistical correspondence	0.1028	0	0.1028
Distribution of particles according to curve II (Figure 4), of bubbles according to curve I (Figure 5)	0.04195	0.00354	0.04549
Distribution of particles according to curve II (Figure 4), of bubbles according to curve II (Figure 5)	0.01903	0.00965	0.02868

Equation (13) was used to calculate the dependence of the degree of extraction m/m_0 of barytes into foam on time, for the above formation of aggregates from particles and bubbles.

Figure 6 shows [t, m/m_0]: curve I for statistical correspondence between the distribution of particles and bubbles, curve II, when the particle distribution curve is displaced in the direction of larger volumes (second process), and curve III, when the bubble distribution curve is displaced in the direction of smaller volumes (third process).

The kinetics of transfer of solid to foam is decreased if a deviation occurs from conditions of statistical correspondence between the distributions of particles and bubbles.

SUMMARY

1. An analogy is established between the influence of particle dimensions and of bubble volume on the type of aggregates formed from them. Each particle has a certain range of volumes of bubbles adhering to it, and each bubble has a range of dimensions of adhering particles in the process of formation of mineralized bubbles. Both ranges become wider as the wettability of the solid particles decreases.

2. A method is developed for calculating the transfer of solid particles into the foam for any size distribution of particles and volume distribution of bubbles.

3. The greatest probability of transfer of solid into the foam is reached in conditions of statistical correspondence between the distributions of particles and bubbles. Deviation from conditions of statistical correspondence by displacement of the particle distribution curve in the direction of larger dimensions, and of the bubble

distribution curve in the direction of smaller volumes lowers the probability of separation of the solid into the foam, and decreases the kinetics of the process.

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MECHANISM OF FORMATION OF FILMS FROM DISPERSIONS OF HIGH POLYMERS

VI. RELATION BETWEEN THE PHYSICO-MECHANICAL PROPERTIES OF DISPERSION FILMS AND THEIR STRUCTURE

S. S. Voyutsky and B. V. Shtarkh

On the basis of the general views accepted by us in the examination of the mechanism of formation of films from dispersions [1], it is not difficult to put forward general suppositions concerning the relationship which should exist between the structure of dispersion films and their physico-mechanical properties.

Films in which cohesion of the globules is far advanced and the heterogeneity of which is low should greatly resemble in properties polymer films obtained from solution or by mastication. Films with a closed structure of the second type should have lower strength and elasticity because of their inhomogeneity. Films with an open structure, which consist of two interpenetrating networks of polymer and emulsifier, should be weaker still, as in this case the polymer globules adhere together only in separate regions. Finally, films with a closed structure of the first type should be near to films of pure emulsifier in their properties. It may therefore be expected that increase of emulsifier or stabilizer content in the latex should produce a deterioration in the mechanical properties of the films. This is confirmed by experiment.

Figure 1 shows variations of the tensile strength of films made from latex DVKhB-70 with different amounts of stabilizer, sodium oleate, added to the latex. The films were obtained by simple drying of the latex at 60° in glass cells. It is seen that the tensile strength decreases with increase in the stabilizer content.

It should be noted that a decrease of film strength with an increase of stabilizer content of the dispersion is not always observed. For example, when additional amounts of the emulsifier contained in latex SKS-30 are introduced, the decrease of film strength is very small, while when ammonium caseinate is added to Revertex even an increase of tensile strength is observed accompanied by an insignificant decrease of the elongation at break. This can be seen in Figure 2, which shows variations of both these properties in Revertex films obtained by drying at 60°, with different amounts of caseinate added to the Revertex. The increase of strength in this case is explained by the fact that caseinate can have a reinforcing effect on the polymer, or can form stable three-dimensional networks in the film, increasing its strength.

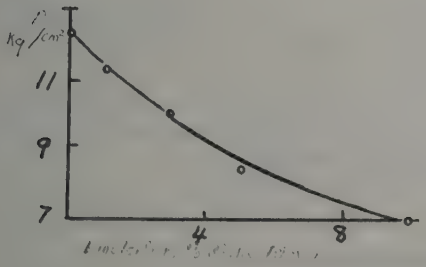

Fig. 1. Dependence of the tensile strength P on the amount of sodium oleate added, for films from latex DVKhB-70.

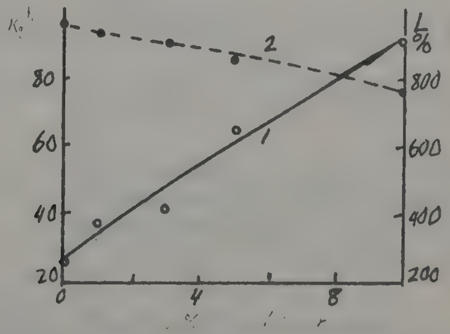

Fig. 2. Tensile strength P (1) and elongation at break L (2) of Revertex films for different contents of ammonium caseinate.

On the basis of our views, increase of the temperature of film formation should increase the strength of dispersion films as the result of increased autohesion and improved cohesion of the globules with each other. We noted this already in 1940 in a discussion of the effect of temperature on the strength of films from polyvinyl chloride dispersions [1].

In the case of latexes, the globules of which have a relatively high power of mutual cohesion, the effect of temperature of film formation on film strength is not so pronounced as in the case of polyvinyl chloride dispersions, but it always exists. This can be seen from Figure 3, which shows changes of the tensile strength of films from latexes SKS-30 and DVKhB-70 with changes of temperature of film formation. Figure 3 also shows that the more thermoplastic is the polymer, the greater is the increase of strength with rise of temperature. In addition, our experiments showed that increase of film formation temperature exercises a greater effect with decreasing amounts of stabilizer in the latex.

Figure 3 also shows a curve for tensile strength against temperature of film formation for films made from a solution of a film of latex SKS-30 in benzene (a similar curve could not be obtained for latex DVKhB-70, as films from this latex did not dissolve in any known solvent). It is seen that in this case the temperature of film formation has very little effect on film strength. This confirms the view that increase of strength of synthetic latex films with increase of temperature of film formation takes place not as a result of changes in the properties of the rubber, but is mainly due to changes in film structure.

The elongation at break of synthetic latex films, according to our experiments, generally increases with rise of film formation temperature, evidently for the same reasons as the tensile strength.

It is important to note that, in the case of Revertex film, strength increases with rise of temperature of film formation up to 20-40°. Further rise of temperature, as can be seen from Figure 4, lowers the strength of Revertex films, apparently as the result of oxidative degradation of natural rubber on heating. As is known, natural rubber, which contains a double bond in the principal valency chain of the molecule, is particularly prone to such degradation [2]. It must be noted that the known fact, that the tensile strength of prepared films is decreased by heating, is in good agreement with the decrease of strength of Revertex films with increased temperature of film formation [3].

On the basis of our views concerning the structure of films, it may be supposed that, because of their heterogeneity, the strength of dispersion films should, as a rule, be less than the strength of the more homogeneous films obtained from solutions. On the other hand, we established in 1940 that the opposite effect is observed in the case of Revertex films [1]. In order to clarify the question of the strength of dispersion and solution films, we investigated the elastico-plastic properties of films made from Revertex and latex SKS-30, and of films made by dissolving the respective latex films and drying the solutions. In both cases the films were made in glass cells at room temperature.

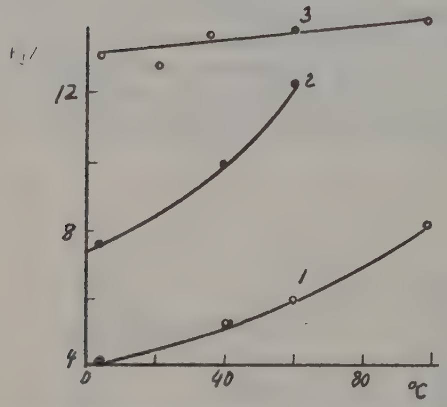

Fig. 3. Effect of temperature of film formation on the tensile strength P: 1 – film from latex SKS-30; 2 – from latex DVKhB-70; 3 – from benzene solution of a film from latex SKS-30.

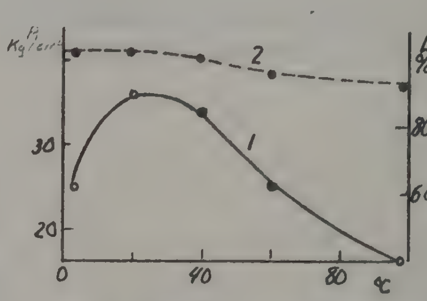

Fig. 4. Effect of temperature of film formation on 1 – tensile strength P; 2 – elongation at break L, of Revertex films.

Figure 5 shows the extensibility curves of the films obtained. The shapes of the curves indicate that only the Revertex film and the film from a solution of Revertex film in benzene have high elasticity. The extensibility

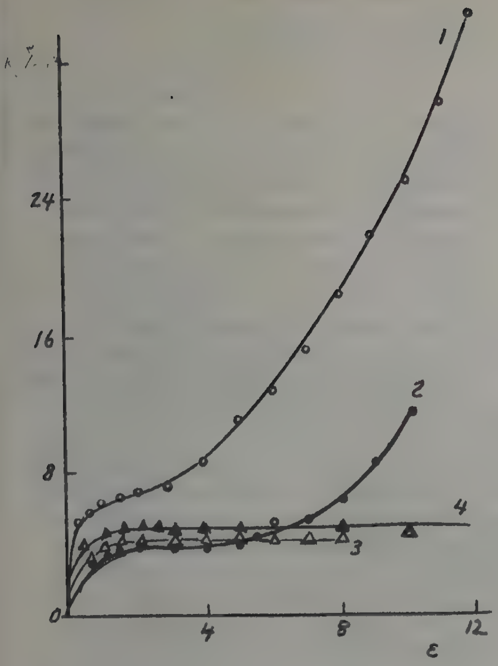

Fig. 5. Extensibility, σ ϵ diagrams for films: 1–Revertex; 2–from a solution of the same film; 3–latex SKS-30; 4–from a solution of the same film.

curve for the Revertex film lies considerably above that of the solution film. This indicates that the first film is much stronger than the second.

The extensibility curves for films from latex SKS-30 and from a solution of this film in benzene do not have the S-shape characteristic of materials with high elasticity. It is seen, however, that the dispersion film is weaker than the solution film. The fact that the elongation at break of the solution film is considerably greater than that of the latex film is particularly striking.

Figure 6 shows curves for changes of the extensibility modulus with deformation of the films. It is seen that, both in the case of Revertex film and the corresponding solution film, the extensibility modulus decreases at first and then increases, and the curve for Revertex film lies somewhat above that of the solution film. It should be noted that variation of the modulus according to a curve with a minimum is characteristic also for rubber films obtained by other methods [2].

In the case of films from SKS-30 latex, the modulus rapidly decreases with increasing deformation and then becomes zero, which is explained by flow of the specimen. The same changes in the modulus are also observed in the deformation of the corresponding solution films. From these results it may be concluded that certain film properties are influenced more by the nature of the high polymer from which the film is made than by the structure of the latter.

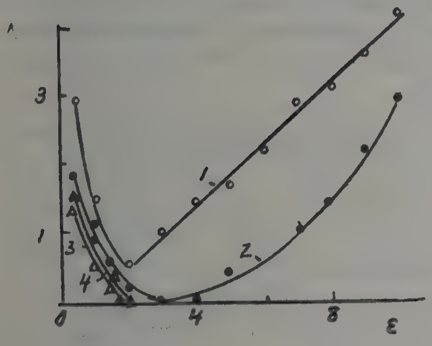

Fig. 6. Dependence of the extensibility modulus E on the deformation ϵ, of films: 1–from Revertex; 2–from a solution of the same film; 3–from latex SKS-30; 4–from a solution of the same film.

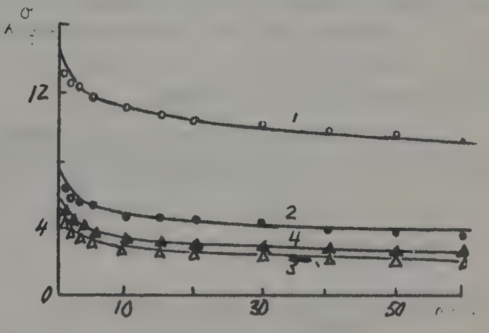

Fig. 7. Relaxation curves for films: 1–from Revertex; 2–from a solution of the same film; 3–from latex SKS-30; 4–from a solution of the same film.

Figure 7 shows relaxation curves for films made from latex SKS-30 and Revertex, and from solutions of the respective films in benzene. The tests were carried out by stretching the films 500%, at room temperature. The table shows the percentage of decrease of stress in the films during 60 minutes in the stretched state.

The table shows that the dissipation of stress differs in different latex and solution films. In the case of Revertex film, the relaxation is less than for the corresponding solution film. The opposite is found in the case

TABLE

Decrease of Stress in Films during 60 Minutes in the Stretched State

Films	Decrease of stress in 60 min, as % of initial
Revertex film	49.6
Film made from a solution of the above in benzene	63.0
Latex SKS-30 film	69.0
Film made from a solution of the above in benzene	67.5

of film from latex SKS-30 and a film from a solution of this in benzene. It is also seen that films of natural rubber, irrespective of the method of preparation, show less relaxation than films of SKS-30 rubber.

All the above once again proves convincingly that films of the same composition may differ substantially in their physico-mechanical properties depending on whether they are prepared from a dispersion or from a solution. However, it is not possible to draw a single conclusion in favor of one or other type of film. For example, films from Revertex have greater strength and elasticity than films from solutions of these films in a volatile solvent, while the reverse is observed in the case of SKS-30 latex. We are inclined to attribute this to the different nature of the emulsifier in the latex.

The protein present in Revertex is either capable of reinforcing the rubber or, being itself capable of forming a strong film, is distributed in the Revertex film in the form of a three-dimensional network and so reinforces it. In the case of latex SKS-30, which contains an emulsifier of a quite different nature, the latter apparently has an unfavorable effect on the autohesion of the rubber globules, which leads to a lower strength of the latex films in comparison with the solution films.

SUMMARY

1. It is shown that, as a rule, decrease of the emulsifier or stabilizer content in dispersions decreases film strength as the result of worse cohesion of the globules and increased heterogeneity of the films. However, film strength is increased by the addition of ammonium caseinate to the dispersion, apparently because caseinate can reinforce the substance of the disperse phase or can form three-dimensional structures in the film and thus reinforce it.

2. It is shown that, as a rule, increase of the temperature of film formation increases the strength of dispersion films, apparently because of better cohesion of the globules and increased homogeneity of the films. The increase of the temperature of film formation has an increasingly greater effect with greater thermoplasticity of the polymer and smaller content of stabilizer in the dispersion. For Revertex, an increase of the temperature of film formation above 20-40° leads to a decrease of tensile strength of the film, apparently because of the greater tendency of natural rubber to oxidation.

3. It is established that dispersion films may be either stronger or weaker than solution films, depending on the nature of the stabilizer present in the dispersion.

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* See Consultants Bureau Translation, page 85

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INVESTIGATION OF THE AGGREGATION OF CASEIN PARTICLES BY THE LIGHT SCATTERING METHOD

P. F. Dyachenko and I. N. Vlodavets

Variation in the degree of dispersion of casein by the influence of various physico-chemical factors plays a significant part in the technology of industrial processing of milk. Study of the processes concerned is complicated by the fact that, on the one hand, the size of the protein particles in milk is considerably below the resolving power of normal microscopes, and, on the other, the size is so great as not to permit the use of the usual methods of molecular weight determination, such as osmometry. In a search for a method for determination of the degree of dispersion, which could be used to study the aggregation processes of casein particles, we selected the light scattering method.

Method for the determination of the mean particle weight of casein. While the light scattering method is in the majority of cases used for determining the size of particles, the diameter of which is considerably less than the wave length of light, there are attempts to apply it to systems consisting of larger particles. An example is the investigation of the dispersivity of synthetic latexes carried out by Yurzhenko and Gusyakov [1]; the average diameter of the latex particles, which they determined by the light scattering method, was from 600 to 1200 A and higher.

As is known, the Debye formula [2] is valid for very dilute solutions under the condition that the particle diameter is considerably less than the wave length of light, λ, and that the refractive index of the dissolved substance, n_1, differs significantly from the refractive index of the solvent, n_0:

$$\tau = HcM, \tag{1}$$

where M is the weight-average molecular (particle) weight of the solute; c is the concentration by weight of the solute in the solution; τ is the extinction coefficient due to light scattering; H is a constant equal to :

$$H = \frac{32\pi^3 n_0^2}{3\lambda^4}\left(\frac{\partial n}{\partial c}\right)^2 \frac{1}{N}, \tag{2}$$

where N is the Avogadro number and $\frac{\partial n}{\partial c}$ is the concentration decrement of the refractive index of the solution $\underline{n}$.

If the suspended particles have dimensions which are not very small compared with the wave length of light, formula (1), which is based on the assumption that the induced vibrations of the electric charges in the particle under the action of the electric field produced by the light source may be considered to be vibrations of the electric dipole, ceases to be valid. Neglect of this in cases when the average particle size exceeds 1/ 5 λ causes a significant error and may lead to incorrect conclusions.

The use of the strict theory of Mie [3], which takes into account, in addition to vibrations of the electric dipole, also vibrations of the magnetic dipole, and vibrations of electric and magnetic quadripoles, octupoles, etc., leads to considerable difficulties in calculation.

Let I_0 be the initial intensity of the light beam, I the intensity of the same beam after passing a path $\underline{1}$ in a turbid medium, then:

$$\tau = \frac{1}{\underline{1}} \ln \frac{I_0}{I} \tag{3}$$

The value of τ so determined may be used to calculate the mean particle weight and average particle size from the formula

$$\tau = H'c\ M, \tag{4}$$

which is valid at fairly high dilutions; however, for fairly large particles the value of H' will not be constant;

it will itself be a function of the particle size, or, more accurately, a function of the parameter $z = \frac{4\pi d}{\lambda}$ where d is the particle diameter.

We may represent H' in the form

$$H' = H\phi(z) \tag{5}$$

where H has a value corresponding to formula (2); $\phi(z)$ is a correction factor which depends on the particle size.

For a monodisperse sol in which the refractive index of the disperse phase differs little from the refractive index of the medium, Mie's strict formulas may be replaced by approximate formulas, derived by Shifrin [4] with the aid of the integro-differential equation method.

The scattering coefficient, calculated for a single spherical particle, is given as a first approximation by the formula

$$k'_p = \frac{\pi d^2}{4} |\alpha|^2 \cdot F'(z), \tag{6}$$

where α is the polarizability; d is the particle diameter; F'(z) is a function of the parameter $z = \frac{4\pi d}{\lambda}$, expressed analytically as follows:

$$F'(z) = \frac{2\pi^2}{z^2}\left[\frac{z^4}{4} + 5z^2 + (4z^2 - 16)(\mathrm{Ci}z - \ln z - c) - 2z \sin z + 14(\cos z - 1)\right] \tag{7}$$

The symbol Ciz is used to denote the integral cosine of z:

$$\mathrm{Ci}z = -\int_z^{\infty} \frac{\cos t}{t}\, dt.$$

The Euler constant C = 0.577 ...

For small particle sizes, formula (6) becomes

$$k_p^0 = 0.183\, z^4 \cdot \frac{\pi d^2}{4} \left|\alpha\right|^2 \tag{8}$$

To find the correction coefficient $\phi(z)$, it is sufficient to find the ratio of the right hand sides of formulas (6) and (8):

$$\phi(z) = \frac{k'_p}{k_p^0} = \frac{F'(z)}{0.183 z^4} = 5.46 \frac{F'(z)}{z^4} \tag{9}$$

Using Shifrin's tables for the function F'(z), it is possible to calculate the values of $\phi(z)$ for different particle diameters. According to Shifrin, use of the first approximation is permissible for systems with $\frac{n_1}{n_0} = 1.3$, up to values of z = 20. For casein hydrosols, $\frac{n_1}{n_0} \approx 1.2$ (see, for example, [5]), and therefore the applicability limits are even somewhat wider.

The diameter d of a spherical casein particle is related to the particle weight M by the following obvious relationship:

$$d = \sqrt[3]{\frac{6M}{\pi \rho N}} \tag{10}$$

Taking the density $\rho = 1.3$, we have

$$d = 1.342 \sqrt[3]{M} \cdot 10^{-8} \text{ cm} \tag{11}$$

On the other hand, we have from formulas (4) and (5):

$$M\phi(z) = \frac{\tau}{Hc} \tag{12}$$

Table 1 shows the results of calculations with formula (12), which establish a relationship between the particle diameter d, the particle weight M, and the value $\frac{\tau}{Hc}$. The table is valid for monodisperse sols and makes it possible to calculate the particle diameter and weight from light scattering measurements for such sols.

TABLE 1

Relationship between Particle Diameter d, Particle Weight M, and the Value $\frac{\tau}{Hc}$ for Dilute Aqueous Solutions of Casein for $\lambda = 5461$ Å

d in Å	$M \cdot 10^{-6}$	$\frac{\tau}{Hc} \cdot 10^{-6}$	d in Å	$M \cdot 10^{-6}$	$\frac{\tau}{Hc} \cdot 10^{-6}$
0	0	0	1653	1843	1297
435	33	32	1740	2149	1461
522	58	57	1958	3063	1896
609	92	85	2175	4198	2351
696	137	131	2610	7254	3272
783	196	180	3045	11519	4135
870	269	244	3480	17105	4960
957	358	318	3915	24349	5795
1044	464	404	4350	33584	6683
1131	590	501	4785	44560	7709
1218	737	607	5220	58033	8705
1305	907	726	5655	73783	9740
1392	1100	854	6090	92153	10690
1479	1320	998	6525	113338	11674
1566	1567	1145	8700	268670	16389

As was shown by ultracentrifuge studies [6-9] and electron microscopy [10,11], casein sol in defatted milk is polydisperse.

It can be easily seen that for a polydisperse sol consisting of a mixture of particles of different particle weight M_i, when v_i is the number of particles of the i type in unit volume, formula (12) will have the following form:

$$\frac{\tau}{Hc} = \frac{\Sigma v_i M_i^2 \phi_i}{\Sigma v_i M_i}, \qquad (13)$$

summated for particles for all types.

The mean particle weight calculated from formula (12) is equal to:

$$\bar{M} = \frac{\Sigma v_i M_i^2 \phi_i}{\phi(\bar{M}) \Sigma v_i M_i} \qquad (14)$$

Leviton and Haller [5] term this value the optical weight-average molecular weight. In the case when $\phi_i \approx \phi(\bar{M})$ for all types of particles may be taken as constant (for a narrow distribution range or for a sufficiently low particle size, when the Rayleigh equation is valid, and therefore $\phi = 1$, equation (14) becomes the usual expression for the weight-average particle weight:

$$\bar{M} = \frac{\Sigma v_i M_i^2}{\Sigma v_i M_i} \qquad (15)$$

The optical weight-average particle weight and the corresponding particle size are independent characteristics of a polydisperse system, which do not depend on the type of the distribution function. Despite a certain conditional nature of these characteristics, they are quite sufficient for the study of processes which are accompanied by changes in the particle sizes of casein.

To determine their practical applicability, it was first necessary to compare particle sizes found by light scattering measurements with those determined by other methods.

To find the value of H, necessary for the calculation of the optical weight-average weight by formula (12), special measurements were made of the concentrational decrement of the refractive index of casein, $\frac{\partial n}{\partial c}$.

Data obtained from 8 samples of pure casein, with corrections for ash and moisture content, gave the value $\frac{\partial n}{\partial c} = 0{,}192$. The close value of $\frac{\partial n}{\partial c} = 0{,}195$ is obtained by a recalculation of Perov's data [12,13].

Thus, the following values of the terms in formula (2) were used for the calculation of H: $\lambda = 5{,}46 \cdot 10^{-5}$; $\frac{\partial n}{\partial c} = 0{,}192$; $N = 6{,}02 \cdot 10^{23}$; $n_0 = 1{,}333$; therefore, $H = 4{,}05 \cdot 15^{-6}$.

Light transmission measurements were carried out with the aid of a differential photoelectric apparatus [14]. A mercury lamp was used as light source; with the use of liquid light filters radiation of the wavelength λ = 5461 Å was obtained. The selenium photocells were connected according to a differential scheme, which permitted the determination of the ratio of the initial intensity of the light I_0 to the intensity $\underline{I}$ of the light after passage through a vessel with the liquid. The layer of liquid between the plane parallel walls of the vessel had a thickness $\underline{l}$ = 13.2 cm. The capacity of the vessel was about 2 liters. Isothermal conditions were ensured by passing a stream of water from an ultrathermostat through special spirals immersed in the vessel. A constant temperature with an accuracy of ± 0.1° was maintained, with the use of a mechanical stirrer and a thermometer, throughout the whole volume of the liquid.

With this apparatus it was possible to carry out continuous observations of changes in the light transmission of the solutions in the temperature range from 5 to 90°. The accuracy of determination of the extinction coefficient τ was about ±2%. The minimum values of the extinction coefficient which could be determined with this apparatus were $\sim 5 \cdot 10^{-5}$ cm^{-1}.

To investigate the possibilities of this apparatus, determinations of the optical weight-average particle weight of casein in natural milk were carried out. The sample of milk was subjected to threefold separation. Exactly 5 ml of the defatted milk was poured into a measuring vessel containing 1500 ml of water or of 0.01 M $CaCl_2$ solution at 20°. The galvanometer deviation was noted 3 minutes after the addition. Because the stirrer acted continuously the liquid in the vessel was sufficiently mixed during this time; at the same time no observable change in the optical density of the solution took place. With this experimental technique, the results obtained on dilution of defatted milk with water were practically the same as the results obtained on dilution with a weak (0.01 M) solution of $CaCl_2$. According to literature data [10,11] in the latter case change of the average particle size takes place more slowly.

Control experiments on the influence of albumin, globulin, and also traces of fat remaining in the milk after threefold separation showed that the error due to these factors does not exceed the error of the calculation formulas, and may be neglected.

The casein concentration in the original milk was determined both by the usual Kjeldahl determination of casein nitrogen, and also approximately, by the formaldehyde titration.

From the experimentally found values of $\frac{\tau}{Hc}$ with the aid of Table 2 or of the corresponding graph, the average particle weight M and the average diameter of the casein particles $\underline{d}$ were determined. The average particle weight varied within the limits of 266 to 780 million, and the average particle size from 860 to 1230 Å. As a comparison we may mention that light scattering measurements in the near infrared gave the value of 220 million for the optical weight-average particle weight, which corresponds to 800 Å for the average particle diameter [5]. Electron microscopy gives a value of 800-1200 Å for the diameter of the particles of the quantitatively predominant fraction of casein in defatted milk [10].

Ultracentrifuge experiments also gave 800-900 Å for the diameter of the particles of the predominant fraction [7]. Thus, the light scattering method in the form used by us gives results in good agreement with those obtained by other known methods for determining the degree of dispersion of casein.

Changes of the Mean Particle Weight of Casein Associated with Variations of Hydrogen Ion Concentration.

The chief advantage of the light scattering method for studying processes accompanied by changes in the degree of dispersion is, as noted by Shifrin [4], that the process of measurement has practically no effect on the substance studied. The use of this method made it possible to study variations of the mean particle weight of casein due to variations in the hydrogen ion concentration.

The casein was prepared from fresh defatted milk by repeated precipitation with dilute hydrochloric acid and alkali according to a technique described previously [15]. The stock solution used was a solution of this product in 0.05 N KOH at pH 9.0, filtered three times through bacterial cardboard, and then through a glass bacterial filter No. 5, 3 times. The concentration of casein in the solution was determined refractometrically. The determination of particle weight of casein in this solution by the light scattering method gave a value of 32000 [15].

This solution was diluted with distilled water to a concentration less than 10^{-4} g/ml in order to retard coagulation processes and render them susceptible of observation. The hydrogen ion concentration in the solution was measured by the addition of small amounts of 0.1 N solutions of HCl or KOH. The acid or alkali was added with continuous stirring of the solution by a mechanical stirrer at constant temperature. The pH was measured with an electronic potentiometer with the aid of a glass electrode.

The light scattering of the solution was measured with the aid of a differential photoelectric apparatus. The results of the measurements were expressed in terms of units of the optical weight-average particle weight.

Figure 1 shows the variation, with time, of the mean particle weight of casein in solution at a concentration of c = $3.8 \cdot 10^{-5}$ g/ml, and pH 5.9, after the pH value had been taken to 5.3 by the addition of 0.1 N solution of HCl.

According to Smoluchowsky [16], the total number of colloidal particles in unit volume varies according to an equation for a reaction of the second order:

$$-\frac{dv}{dt} = k_1 v^2. \tag{16}$$

By substituting $v = \frac{Nc}{M}$, we find that the mean particle weight should depend on time in the following way:

$$M = M_0 + k_1 Nct \tag{17}$$

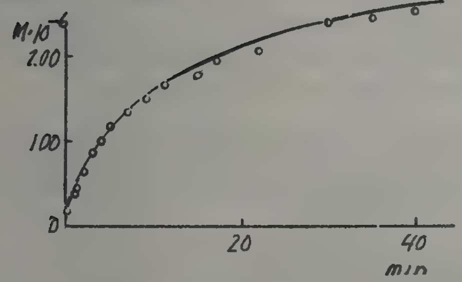

Fig. 1. Kinetics of the variation of the mean particle weight of casein in a solution with concentration $3.8 \cdot 10^{-5}$ g/ml, pH 5.9, after addition of hydrochloric acid to pH 5.3 (at 20°).

If we allow for the reverse process of disaggregation of the particles, which may be described by an equation for a first order reaction:

$$\frac{dv}{dt} = k_2 v \tag{18}$$

the change in the degree of dispersion of a colloidal solution of casein should be described by the following kinetic equation:

$$-\frac{dv}{dt} = k_1 v^2 - k_2 v, \tag{19}$$

integration of which gives the expression:

$$\ln\left(\frac{M_\infty - M_0}{M_\infty - M}\right) = k_2 t \tag{20}$$

In reality this equation is not satisfied. The following equation is satisfied:

$$\ln\left(\frac{M_\infty - M_0}{M_\infty - M}\right) = k\sqrt{t} \tag{21}$$

The curve in Figure 1 is drawn according to equation (21) with the values for the constants of $M_\infty = 350 \cdot 10^6$; k = 0.23. Equation (21) is applicable to the description of all kinetic experiments in which the degree of dispersion of casein varied with time as the result of instantaneous addition of electrolyte. In all cases it was possible, by suitable selection of the constants M_∞ and k, to obtain good agreement with the experimental data.

The aggregation of casein particles, shown in Figure 1, under the action of acid may be regarded as the initial stage of the process of acid coagulation. Approach to the isoelectric point, both from the acid and from the alkaline side, results in a considerable increase of the average particle size.

A series of experiments was carried out to establish the nature of the dependence of the equilibrium value of the mean particle weight of casein on the pH value, the value of M obtained one hour after the addition of acid or alkali being taken, as an approximation, for the equilibrium value of M_{∞}. The experiments were so performed that the change of degree of dispersion took place in one direction, toward an increase in the average particle size, so that the change of pH was always in the direction of an approach to the isoelectric point.

As the result of these experiments the curve shown in Fig. 2 was obtained A characteristic peculiarity of this curve is a fairly sharp maximum of the particle weight at the isoelectric point (at pH 4.6). An analogous curve was once obtained for the dependence of the light scattering of gelatin sols on the pH of the medium [17]. This curve also reflects the corresponding variations in the particle weight, although such calculations were not made by the authors.

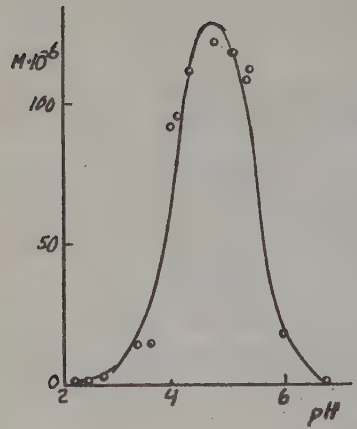

Fig. 2. Dependence of the equilibrium particle weight of casein on the pH value at 20°. The casein concentration in the solution was $3.8 \cdot 10^{-5}$ g/ml.

Changes of the Mean Particle Weight of Casein Associated with Variations of Calcium Ion Concentration.

Casein is present in natural milk mainly in the form of a calcium salt (or, more exactly, in the form of the so-called complex calcium caseinate-phosphate). The discrepancy between the mean particle weight of casein in milk (260 million and higher) and the true molecular weight of casein (32000) which can in no way be explained by the aggregation of particles by the effect of increased acidity of the medium (pH of fresh milk is 6.7), leads to the view that the presence of calcium ions is the basic cause of the aggregation of casein particles in milk.

By the use of the light scattering method it was possible to study the aggregation of casein particles in the presence of calcium ions in greater detail. By analogy with pH, we use the designation pCa to denote the negative logarithm of the calcium ion concentration. As the binding of calcium ions takes place to a relatively small extent at low concentrations of casein, the value of pCa may be obtained directly from the amount of $CaCl_2$ added. The curve in Figure 3 shows the variation in the degree of dispersion of casein after alteration of pCa from 3.27 to 2.75. The kinetics of this process is also described by equation (21), and the curve in the figure is calculated from this equation for the values of $M_{\infty} = 780 \cdot 10^{6}$ and $k = 0.28$.

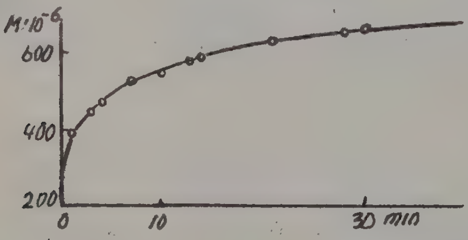

Fig. 3. Kinetics of the variation of the mean particle weight of casein in a solution with concentration $2.25 \cdot 10^{-5}$ g/ml, pH 6.7, pCa = 3.27, after addition of $CaCl_2$ to pCa = 2.75 at 80°.

The opposite process of a decrease in the mean particle size of casein may be observed when milk is diluted with water. Figure 4 shows the kinetics of the disaggregation of casein particles in milk after a 150-fold dilution of defatted milk with water. In this case the kinetic curve may also be represented by equation (21), with the values $M_{\infty} = 28 \cdot 10^{6}$, $k = 0.31$. The experimental points fit this curve well.

The decrease in the mean particle size on dilution of milk with water is apparently the consequence of two factors which act in the same direction: 1) dilution increases the pCa value; 2) decrease of the casein concentration displaces the equilibrium in the direction of formation of smaller particles.

In order to determine the role of the first factor as definitely as possible, a series of experiments was carried out to study the effect of additions of calcium chloride to dilute solutions of pure casein on the mean particle size. In order to obtain values as near to equilibrium as possible, measurements of mean particle size were made each time 40 minutes after the addition of $CaCl_2$ solution. To avoid visible coagulation, and also to decrease the error in pCa determination which results from combination of Ca^{++} with the protein, the measurements were carried out in very dilute solutions of casein, of a concentration of $1.8 \cdot 10^{-5}$ g/ml.

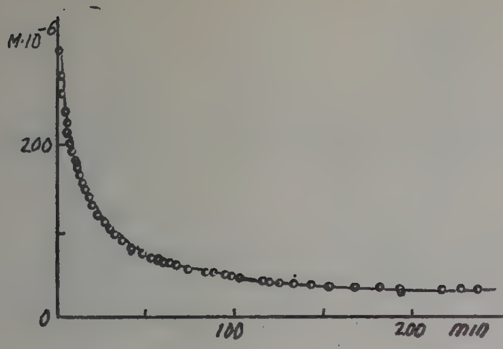

Fig. 4. Kinetics of the variation of the mean particle weight of casein in defatted milk after 150-fold dilution with water (at a casein concentration of $1.72\cdot10^{-4}$ g/ml at 20°.

The results of this series of experiments are shown in Figure 5. As Figure 5 shows, the variation of mean particle weight with pCa resembles the variation of particle weight with pH which is shown in Fig. 2. The particle weight of casein has a maximum value at pCa $\sim$1.5. Both an increase and a decrease in the calcium ion concentration lead to a decrease in the size of protein particles.

The impression is obtained that the position of the maximum in this case corresponds to the isoelectric point. This question, however, cannot be finally settled on the basis of data on particle size only. In cases when calcium ions are selectively combined with certain functional groups, such as phosphoric acid groups, the aggregation maximum may be associated only with the saturation of these specific groups and need not necessarily correspond to the isoelectric state of the casein molecule as a whole. This view is supported by the fact that decrease of pH (approach to pH 4.6) results in a further increase in the mean particle size not only in the region of pCa (pCa >2), where binding both of hydrogen ions and of calcium ions undoubtedly leads to a decrease of negative charge, but also in the region of pCa (pCa <1.5), where an increase in the calcium ion concentration leads to disaggregation of the particles (Figure 6).

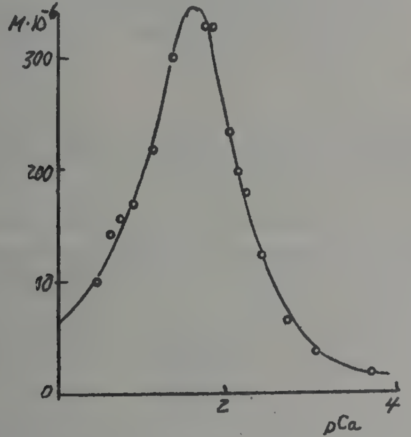

Fig. 5. Dependence of the equilibrium particle weight of casein on the pCa value (pH 6.0, casein concentration $1.8\cdot10^{-5}$ g/ml) at 40°.

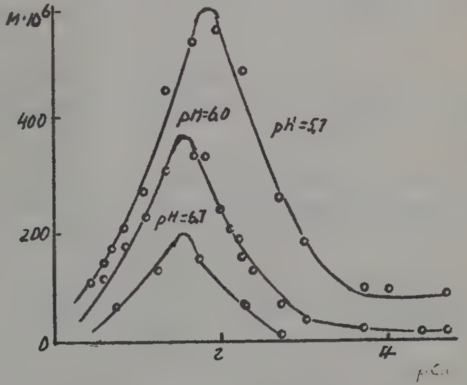

Fig. 6. Effect of the pH value on the dependence of the mean particle weight of casein on the pCa value in a solution of pure casein (concentration $1.8\cdot10^{-5}$ g/ml) at 40°.

We also studied the dependence of the mean particle weight of casein on the concentration of the protein itself. Figure 7 shows the dependence of the mean particle weight of casein on the concentration of the protein itself at various values of pCa. The measurements were carried out with the aid of a photoelectric apparatus at 40°. The initial pH value of all the solutions was 6.7.

It follows both from the equation for reversible aggregation (19) and from the empirical equation (21) that, at constant concentration of calcium ions and constant pH value, the mean number of particles per unit volume, v_∞, should be a constant value for the equilibrium state, independent of the concentration of casein. Accordingly, the mean particle weight of casein under other equal conditions should be proportional to its concentration by weight in the solution. As Figure 7 shows, despite some scattering of the experimental points, which is to be explained by the approximate nature of the determination of equilibrium values, in general,

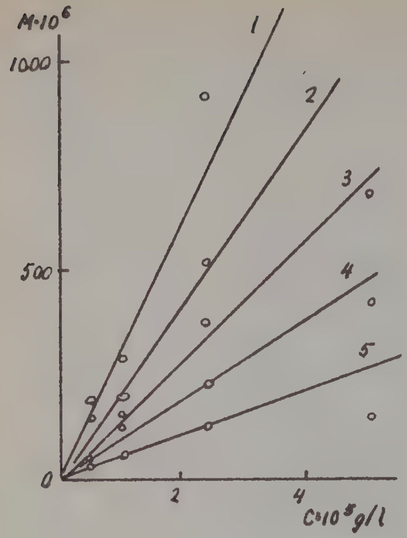

Fig. 7. Dependence of the mean particle weight on the concentration of casein at pCa values: 1 – 1.5; 2 – 1.8; 3–2.08; 4–2.3; 5 – 2.8; temperature 40°, pH 6.7.

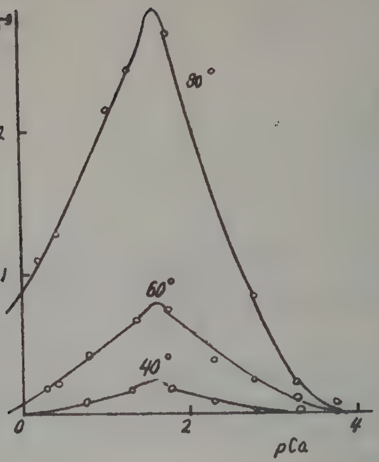

Fig. 8. Dependence of the mean particle weight of casein on the pCa value at different temperatures. Concentration of casein $2.3 \cdot 10^{-5}$ g/ml, pH 6.7.

a proportionality is maintained between the mean particle weight and the weight concentration of casein at equal pCa values.

The influence of temperature on the dependence of the mean particle weight of casein on pCa is shown in Figure 8. Increase of temperature leads to an increase of the mean particle weight of casein at any value of pCa. This leads to the conclusion that the combination of calcium ions with casein is endothermic in character.

The laws found by the light scattering method for the behavior of casein solutions in presence of calcium ions are generally valid also for milk. The difference is only that, first, the concentration of calcium salts in milk is usually fairly considerable even without extraneous additions (it corresponds to pCa values from 3.0 to 2.0) and therefore the mean particle weight of casein in normal milk does not decrease below several hundred millions; second, the existence of a maximum on the curve for the dependence of mean particle weight on pCa can be established only at relatively low temperatures (approximately to 40°). At higher temperatures, due to the high concentration of casein in milk, coagulation is observed in the region of maximum aggregation of the particles, accompanied by complete destruction of the colloidal system. However, an increase in the solubility of casein with an increase in the concentration of calcium chloride may be observed here also. These results, which confirm that our views on the behavior of casein solutions are applicable to natural milk, are in full agreement with Ionin's observations [18], who noted that while the addition of small amounts of calcium chloride to milk accelerates its "gelatinization" on warming, the addition of amounts in excess of 8 g/liter has a retarding effect, and the temperature threshold of coagulation on further increase of the calcium ion concentration is shifted into the region of higher temperatures.

Study of the aggregation process of casein particles in the presence of calcium ions has made it possible to commence the development of a new method for the industrial extraction of proteins from defatted milk based on the addition of calcium chloride to the milk and the action of elevated temperatures on the milk [19].

SUMMARY

1. A method is described for the determination of the "optical weight-average particle weight" of casein, based on measurements of the transparency of dilute solutions of the protein in monochromatic light of wavelength 5461 Å, with the aid of a differential photoelectric apparatus. The results obtained by this method (mean particle weight from 266 to 780 million, mean diameter of casein particles in defatted natural milk from 860 to 1230 Å) are in agreement with literature data obtained by the electron microscope and ultracentrifuge methods.

2. The kinetics of variation of the mean particle weight of casein with changes in the concentrations of hydrogen and calcium ions may be described by the empirical equation

$$\ln\left(\frac{M_\infty - M_0}{M_\infty - M}\right) = k t^{1/2}$$

where M is the particle weight (M_0 is the initial and M_∞ the equilibrium value); t is the time; k is a constant. This equation differs from the equation which follows from Smoluchowsky's theory for reversible coagulation in the exponent of t.

3. The curves for the dependence of the equilibrium values of the mean particle weight of casein on pH and pCa have sharp maxima at pH $\approx$ 4.6, and, correspondingly, at pCa $\approx$ 1.5. In more concentrated solutions of casein and in natural milk these maxima correspond to regions of visible coagulation (in the case of addition of $CaCl_2$, at temperatures above 40°).

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* See Consultants Bureau Translation, page 153

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DENATURATION OF VEGETABLE PROTEINS BY DETERGENTS AND CAUSTIC ALKALI

N. F. Ermolenko and D. Z. Ginzburg

Proteins present a great interest as high polymer substances of an amphoteric nature which have a great biological and technical significance. A specific property of proteins is the ability of their macromolecules to undergo denaturation under definite conditions, which significantly affects a number of properties of proteins, and particularly their solubility.

Among views on the mechanism of protein denaturation particular attention is merited by the views developed by Talmud, Bresler, Pasynsky, and others [1], according to which denaturation is the result of a change in the configuration of the protein macromolecules under the influence of a number of factors which lead to an increase in their asymmetry (b/a), often several fold. According to these views the protein macromolecules are polypeptide chains with lateral polar and nonpolar groups, which are situated on both sides of the principal valency chain in a definite sequence.

Under definite conditions (nature of the medium, temperature), the principal valency chain can become convuluted into a spiral-like globule, in which a hydrophobic nucleus is formed as the result of the approach of the hydrophobic side chains, while the polar hydrophilic groups face outward and form the surface of the globule. Under the influence of the medium a change may take place in the action of the intermolecular forces leading to partial rupture of the bonds between individual groups in the globule, which results in a partial uncoiling of the globule to some equilibrium state, which is determined by the equilibrium between the intermolecular forces which act in the system.

On this basis the shape of the globule and its degree of asymmetry should vary with change of composition, and accordingly, of the properties of the medium, and this variation should be fully reversible. The shape of the protein globule in solution will depend on the equilibrium between the forces of cohesion and repulsion within the molecule. When the equilibrium is disturbed the macromolecule will undergo deformation. Therefore, for denaturation, it is necessary for a certain minimum number of bonds in the molecule to be broken, which leads to partial uncoiling of the globule.

Uncoiling of the globule leads, on the one hand, to an increase in the energy as the result of contact of the hydrophobic groups with the polar medium, water; and, on the other, to an increase of entropy due to an increase in the number of statistically possible configurations of macromolecules. In a certain new equilibrium state the two factors compensate each other.

Denaturation changes in proteins are observed by changes in a number of physico-chemical and other properties: changes of viscosity, solubility, numbers of sulfhydryl groups, changes in dye absorption, etc. In the present instance, we studied the denaturation of the vegetable protein of the lupin by the action of detergents and alkali.

EXPERIMENTAL

The denaturation of vegetable protein was studied on protein from the blue lupin (Lupinus angustifolius). The denaturating agents were detergents - Sulfanole and Igepon T [$CH_3(CH_2)_7CH{=}CH(CH_2)_7CONHCH_2CH_2SO_3Na$], and alkali.

The protein was dissolved in a buffer mixture (borate buffer, pH 10.0). The solution was mixed thoroughly and left 20 hours at room temperature. Then either water, or a detergent solution of the corresponding concentration in the same volume, was added to separate portions of the protein solution (see table).

TABLE

Variation in the Asymmetry of Vegetable Protein Molecules under the Influence of Detergents

Blue Lupin Protein

Solvent	Amount of solvent in %	Concentration of protein in g/cm^3	$\varphi \cdot 10^3$	$\frac{\eta}{\eta_0}$	K	b/a
Water		0.005	4	1.029	7.3	6.2
Igepon T	0.5			1.043	10.8	8.4
Igepon T	2.5			1.051	12.9	9.6
Sulfanole	5.0			1.043	10.7	8.3
Sulfanole	10.0			1.046	11.5	8.8
Water		0.0075	6	1.047	7.9	6.6
Igepon T	0.5			1.063	10.5	8.2
Sulfanole	5.0			1.069	11.4	8.8
Water		0.01	8	1.067	8.34	6.8
Igepon T	0.5			1.086	10.8	8.4
Igepon T	2.5			1.103	12.8	9.6
Sulfanole	5.0			1.095	11.8	9.0
Sulfanole	10.0			1.092	11.4	8.8

Determination of the relative viscosity of protein solutions was carried out in the usual capillary viscosimeter, with an efflux rate for water of 169 " at 25°, 1.5 hours after addition of detergent solution, alkali, or water. The relative viscosity of protein solutions was determined for different concentrations of protein.

The degree of asymmetry b/a was calculated from the constant $K = \eta_{sp}/\varphi$ with the aid of Simha's tables [2] from Kuhn's equation [3]:

$$\frac{\eta}{\eta_0} - 1 = \left[2.5 + \left(\frac{b}{4a}\right)^2\right]\varphi,$$

where $\frac{\eta}{\eta_0}$ is the specific viscosity of the solution; φ is the volume concentration of the protein, equal to the product Vc, the specific volume of the protein and its concentration in the solution.

It is known that complexes are formed between molecules of protein and detergent by forces of molecular interaction, even if the protein and the detergent have charges of the same sign. According to conditions, the molecules of the detergents may direct either their polar or their nonpolar groups toward the protein molecule [4].

As the result of molecular interaction between the molecules of detergent and protein, denaturation changes occur in the latter, which lead to some degree of uncoiling of the globule and to an increase in its degree of asymmetry, which causes a change in the viscosity of the solution.

Our data on the denaturation of lupin protein are shown in the table.

Calculation of the degree of asymmetry of the protein macromolecules from values of the relative viscosity and volume concentration of the protein solutions shows that in presence of Igepon T the value of b/a increases by a factor of about 1.5, which indicates elongation of the globules. The degree of uncoiling of the globules increases with increasing concentration of detergent.

In the presence of Sulfanole, which was used in 5 and 10% concentrations, the degree of asymmetry of the protein macromolecules increases 1.3-1.4 times. Increase of the concentration of Sulfanole in the protein solution from 3 to 10% does not significantly change the solution viscosity and therefore the asymmetry of the protein macromolecules. In the presence of detergents, change of the protein concentration in the range 0.5-1.0% has no significant effect on the value of b/a for the protein macromolecules. As was shown by us earlier [1], the value of b/a for lupin protein macromolecules in 6.0 M urea solution is almost doubled. Therefore, the detergents studied have less denaturing action on vegetable protein than does 6.0 M urea solution.

It is known from the data of a number of workers [5] that the increase in the degree of asymmetry of animal proteins in urea solutions of the same concentration is considerably greater than was found by us for vegetable protein of the lupin. This indicates that the macromolecules of this type of vegetable protein have a more rigid, more stable configuration than the macromolecules of a number of animal proteins.

Denaturation of vegetable protein by caustic alkali. In addition to urea, guanidine, detergents, and other organic compounds, both acids and alkalis have a denaturing effect on proteins. It was shown earlier [6] that when the pH of protein solutions is changed in the acid or the alkaline direction, the viscosity η of such solutions (egg albumin, serum albumin, globulin, gelatin, etc.) increases in both directions from the isoelectric point, which indicates uncoiling of the globules or denaturation of the protein macromolecules.

This behavior of protein molecules is associated with their amphoteric nature, and, consequently, with their ability to react with acids and alkalis through their polar regions, which results in deformation of the molecules or denaturation. The forces which extend the globule in an alkaline medium are due to electrostatic repulsion of similarly charged carboxyl groups, while in an acid medium, on the other hand, repulsion forces come into play between similarly charged amino groups.

Figure 1 shows the variation of the degree of asymmetry, b/a, of protein macromolecules with increase in the alkalinity of the medium. As changes of protein concentration in the limits of 0.5-1.0% have little influence on the value of b/a in the corresponding alkaline media, the curves for variation of b/a of protein solutions with changes of alkalinity of the medium almost coincide, and therefore they had to be shown separately.

As Figure 1 shows, the values of b/a pass through a maximum with increase of alkali concentration, which indicates that as the alkali concentration increases, the protein macromolecules are first stretched, denatured, and at still higher alkali concentrations again begin to become coiled into globules. This is due to the fact that as the alkali concentration increases, the polarity of the medium becomes greater, leading to an increase in the energy of the protein particles, as the nonpolar regions of the extended macromolecules of the protein are in contact with a strongly polar medium. For this reason the protein macromolecules again begin to coil into globules and the value of b/a decreases with increase of alkali concentration.

Protein denaturation and dye adsorption. It is known that denatured proteins take up dye better than do native proteins; in particular, dead and damaged cells, which are denatured to a certain degree, are dyed more intensively than normal, undamaged cells.

Study of serum albumin and globulin showed [7] that the degree of sorption of dyes by these proteins depends on their degree of denaturation, in such a way that the sorption of dye passes through a maximum with increased denaturation. As the molecular structure of vegetable proteins, as we showed above, is more rigid than that of animal proteins, it was important to study the behavior of vegetable protein with dyes as the degree of denaturation of the protein varies; that is, with variations of the values of b/a, determined from the viscosity of the solutions.

We used proteins of the blue and yellow lupins, and studied their adsorption of azobenzene dye before and after denaturation of the proteins by 2.0 and 6.0 M urea solutions.

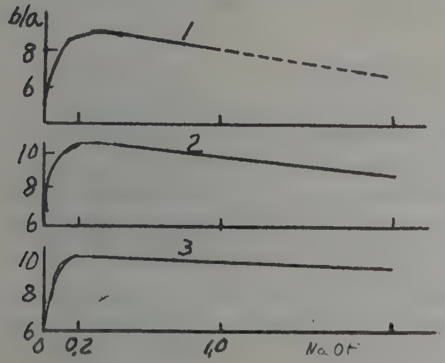

Fig. 1. Variation of the degree of asymmetry of protein macromolecules with increased alkalinity of the medium: 1 — 1.0%; 2 — 0.75%; 3 — 0.5% protein.

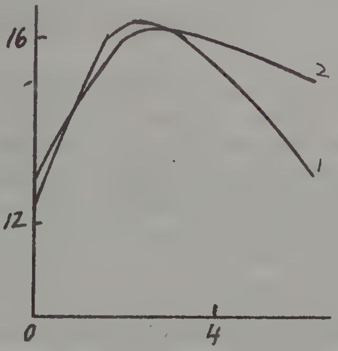

Fig. 2. Adsorption of azobenzene by proteins denatured by urea: 1 — blue, and 2 — yellow lupin.

As is seen from Figure 2, the adsorption of the hydrophobic dye by vegetable proteins denatured by 2.0 and 6.0 M urea solutions, passes through a maximum which corresponds to the denaturation of the protein by 2.0 M urea solution; that is, a certain medium degree of uncoiling of the protein macromolecules during denaturation.

As in the case of animal proteins, the passage of the adsorption of a hydrophobic dye through a maximum with increase of the degree of denaturation of vegetable proteins may be explained by the fact that at a certain medium value of uncoiling of the protein macromolecules, the hydrophobic nucleus of the globule is opened most completely, analogously to a hydrophobic droplet, which in this case adsorbs the hydrophobic dye to a maximum degree.

At lower degrees of denaturation and a lower degree of uncoiling of the globule, its hydrophobic nucleus is less accessible to the dye and the adsorption of the latter by the protein is less. On the other hand, at higher degrees of denaturation and greater uncoiling of the globule, the hydrophobic nucleus becomes smaller, the hydrophobic side chains in the extended macromolecule are situated apart from each other, and binding of the dye by these groups also becomes less.

In the denaturation of proteins by 6.0 M urea solution, the molecular asymmetry b/a of blue lupin protein increases almost twice, and that of yellow lupin protein, 1.2 times. The adsorption of dye by blue lupin protein in these conditions is less than by yellow lupin protein.

Consequently, the less extended macromolecules of the yellow lupin protein have a hydrophobic nucleus of nonpolar side chains, which adsorbs the hydrophobic dye better than the separate hydrophobic side chains, at considerable distances apart, of the considerably extended macromolecules of blue lupin protein.

SUMMARY

1. When vegetable protein from the blue lupin is denatured by detergents – Sulfanole and Igepon T – the degree of asymmetry of the protein macromolecule increases 1.4-1.5 times, which is considerably less than in similar denaturation of animal proteins. This indicates a greater rigidity of the macromolecular chains of vegetable protein.

2. When the same vegetable protein is denatured by caustic alkali, the value of the degree of asymmetry of the protein macromolecules passes through a maximum as the concentration of alkali increases.

3. The degree of sorption of a hydrophobic dye – azobenzene – by vegetable protein varies with variation in the degree of denaturation of the protein. As the protein globule becomes uncoiled in the process of denaturation, the sorption of dye passes through a maximum, which lies in the region of a certain degree of extension of the globule.

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*See Consultants Bureau Translation, page 229.

THE STRUCTURE OF GELS

IV. THE EFFECT OF VARIOUS ADDITIONS ON THE MECHANICAL PROPERTIES OF GELS AND SOLUTIONS OF GELATIN

P. I. Zubov, Z. N. Zhurkina, and V. A. Kargin

In previous communications [1] it was shown that the formation of gels and globular structures is determined by the interaction of the same groups which enter the composition of protein macromolecules. The only difference between the two processes is that gelling is associated with the formation of local bonds between the active groups of different molecules, while in globulization the formation of bonds is effected within the limits of one or a few molecules.

For a better understanding of the mechanism of intermolecular and intramolecular actions, it is necessary to know the nature of the local bonds which determine these interactions. However, at the present time this question cannot be considered as fully solved. Thus, Lipatov [2] considers that gel formation is due to the formation of bonds between hydrophobic regions of the polymer molecules. It follows from our data [1] that both intermolecular and intramolecular interactions in gels and solutions are due to the formation of local bonds, in the first instance between polar groups in the chain molecules of the protein.

The present paper is devoted to a more detailed study of this question. As will be seen in the experimental section, the problem is solved on the basis of a study of the temperature dependence of the mechanical deformation of gels and of the viscosity of dilute solutions of gelatin in the presence of various additions.

EXPERIMENTAL

The gels and solutions of gelatin were prepared and their mechanical properties measured as before [1]. The additions were introduced into the solvent before the air-dry gelatin was dissolved. The viscosities of the solutions were measured in an Ostwald viscosimeter, usually twenty-four hours after preparation of the solutions. The viscosimeter capillary corresponded to the condition of laminar flow (Reynolds criterion in absence of structural viscosity). The relative viscosity of the solution was always determined in relation to the solvent medium.

It was previously shown [1] that in presence of urea the melting point of the gel is displaced into the region of lower temperatures. A similar effect is found when ammonium nitrate is added to the gel (Figure 1). The experiments were carried out with a frequency apparatus [3] at a single rate of deformation (one vibration per minute).

Figure 1 shows that ammonium nitrate, like urea, by weakening the interaction between the chains, displaces the melting temperature of the gel into the region of lower temperatures.

As urea and ammonium nitrate are polar substances, the effect of the additions may be due to the fact that the polar groups of these substances, in acting on the polar groups of gelatin, block them and so hinder the transition of the solution into the gel state. This view is also supported by the fact that additions of acetamide, the molecule of which contains one amino group, have a smaller effect on the mechanical properties of gels than do additions of urea, the molecule of which contains two amino groups.

Figure 2 shows data on the relative deformation of gelatin gels without additions and with additions of acetamide and urea. It is seen from Figure 2 that the deformation of a gel prepared with the addition of acetamide is considerably less than the deformation of a gel prepared in urea solution. The flow process or the transition of the gel into a solution state in presence of acetamide commences at 20°, while in presence of urea this occurs at 10°. It, therefore, follows from these results that it is the polar groups of the additions which are the cause of the rupture of the local bonds.

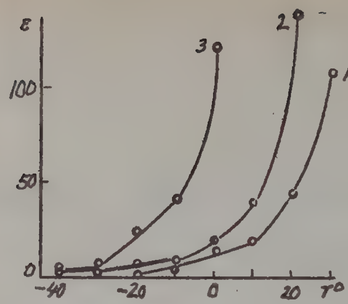

Fig. 1. Deformation of 20% gelatin gels, prepared: 1 – in water; 2 – in 1 M solution of ammonium nitrate; 3 – in 3 M solution of ammonium nitrate.

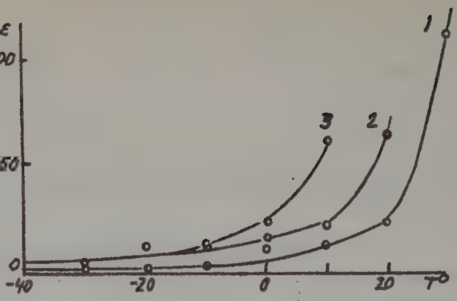

Fig. 2. Deformation of 20% gelatin gels, prepared: 1 – in water; 2 – in 3 M acetamide solution; 3 – in 3 M urea solution.

We carried out experiments on the effects of a number of other additions, apart from urea, ammonium nitrate, and acetamide, on the mechanical properties of 10% gelatin gels. Figure 3 shows comparative data on the deformation of gels prepared in the presence of glycerol, butyl alcohol, glycocoll, calcium sulfate, and barium sulfate. As Figure 3 shows, the greatest deformation was found in the gel prepared without additions. As regards the gels formed from solutions with various additions, it is only possible to state that these additions do not lower the melting points of the gels. Figure 3 shows the values of the relative deformations of gels containing not only nonpolar and weakly polar, but also strongly polar additions: calcium sulfate and glycocoll. It is seen that these additions also do not lower the melting point of the gels. Consequently, not all substances which contain polar groups weaken the local bonds which are formed between the chain molecules of gelatin. For a more complete elucidation of the mechanism of action of additions on intermolecular and intramolecular bonds, an investigation was made of the temperature dependence of the viscosity of dilute solutions of gelatin in presence of different substances.

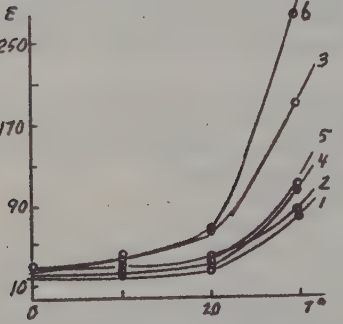

Fig. 3. Deformation of 20% gels of gelatin, prepared in presence of various additions: 1 – glycerol; 2 – n-butyl alcohol; 3 – $CaSO_4$; 4 – $BaSO_4$; 5 – glycocoll; 6 – without additions.

It is seen from the data of Figures 4 and 5 that increase of the concentration of urea, and, to a greater extent, of ammonium nitrate, results in a sharp lowering of specific viscosity. A small number of these substances have no appreciable influence on the viscosity of the solutions. These effects are in full agreement with what was observed by us in studying the effect of these additions on the mechanical properties of gels. It

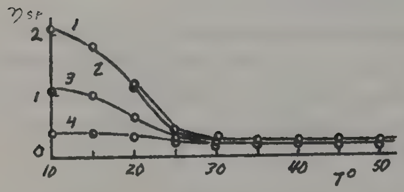

Fig. 4. Specific viscosity of 0.5% solutions of gelatin, prepared: 1 – in water; 2 – in 0.1 M; 3 – in 1 M; 4 – in 3 M solutions of urea.

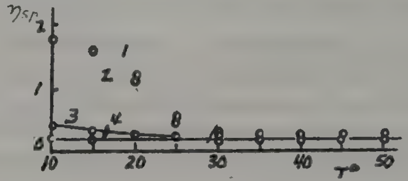

Fig. 5. Specific viscosity of 0.5% solutions of gelatin, prepared: 1 – in water; 2 – in 0.1 M; 3 – in 1 M; 4 – in 3 M solutions of NH_4NO_3.

should be noted that the action of urea and ammonium nitrate affects the local bonds only. No rupture of the chains takes place in presence of these substances. This can be seen even from the fact that above 30° the viscosity is practically the same both in the presence of these additions and in their absence.

Since both additions are polar substances, it may be concluded from these reults and also from data on the deformation of gels that the decrease of solution viscosity and the lowering of the melting point of the gels are both determined by the interaction of these substances with the polar groups of the gelatin chain molecules. Consequently, the local nature of these processes finds its expression in changes of the interaction between the polar groups of the chains.

This assumption, in our view, is in agreement with the structure of the gelatin molecule which, as is known, contains amino, carboxyl, and other polar groups. The presence of these groups determines the basic mechanical properties both of gels and of solutions of gelatin.

In order to modify (weaken) the interaction of the groups which determine the mechanical properties of the gels, it is sufficient to introduce a polar substance into the system. In relation to gelatin, water, above all, is such a substance. However, the dispersing power of water is insufficient to destroy all the bonds in gelatin at temperatures up to 30°. Urea and ammonium nitrate are polar substances which help water to complete the process of destruction of the local bonds.

As Rebinder and Zhigach [4] showed, additions of alcohols in the homologous series from methyl to butyl also lower the viscosity of gelatin solutions. In their analysis of this effect, these authors reached the following conclusion: "when surface active substances (for example, alcohols) are added to an aqueous solution of a hydrophilic colloid, their polar groups become bound to the polar groups of the micelles and so exert a dehydrating effect by decreasing both the surface and the volume solvation, hydrophobization of the hydrophilic micelles takes place, and, consequently, gel formation is hindered."

The same authors showed that 1 g of gelatin in 0.1% gelatin solution absorbs up to 0.018 M of n-butyl alcohol. The dispersing action of urea was tentatively associated with chemical action of the amino groups by these authors.

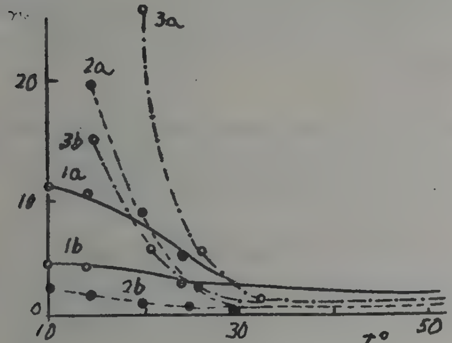

Fig. 6. Specific viscosity of gelatin solutions of the concentration: 1 — 0.5%; 2 — 0.75%; 3 — 1%, prepared a — in water, b — in 5% solution of n-butyl alcohol.

In view of the fact that we did not find a dispersing action of alcohols in studying the mechanical properties of gels, we also measured the viscosity of gelatin solutions in presence of alcohol. Rebinder and Zhigach attributed the action of alcohol on gelatin to surface activity, and therefore we used, as an addition, the most surface active alcohol of this series, n-butyl alcohol. As a comparison with the data of Zhigach and Rebinder, who measured the relative viscosity of 0.5-0.75% gelatin solutions at 20°, we measured the viscosity of 0.5-1% solutions of gelatin in the temperature range of 10-50° (see Figure 6).

From the data of Figure 6 it may be concluded that n-butyl alcohol does have a dispersing effect. However, this effect is less and less pronounced as the concentration of the gelatin solution increases. Thus, even in 1% gelatin solution, prepared in a 1 M, or a practically saturated solution of n-butyl alcohol, the viscosity is comparable to the viscosity without additions. Consequently, we can consider a dispersing effect of alcohols only in the region of dilute solutions of gelatin, in conditions of small numbers of local bonds. These results explain why additions of n-butyl alcohol, as well as of other nonpolar and weakly polar substances, displace the melting point of gels.

In our view, the mechanism of the dispersing action of alcohol on gelatin solutions is quite identical with the mechanism of the action of urea and similar additions. The rupture and weakening of local bonds between the gelatin molecules in the presence of alcohols takes place as the result of sorption of polar groups contained in the alcohol molecules on the polar groups of the gelatin molecules. The rupture of local bonds in presence of urea occurs for the same reason. The only difference is apparently in the extent of the dispersing action, as urea contains the more polar groups.

No special chemical action, such as degradation, is produced by urea or ammonium nitrate. This can be seen from the fact that the viscosity of gelatin in trimolal (Figures 4 and 5) and even in quinquemolal (no figure shown) solutions changes only until the local bonds are destroyed; after this it remains practically the same as in pure solutions of gelatin. Therefore our conclusion that the polar groups of additions present in the solutions determine the decrease in the viscosity of gelatin, remains valid for alcohols.

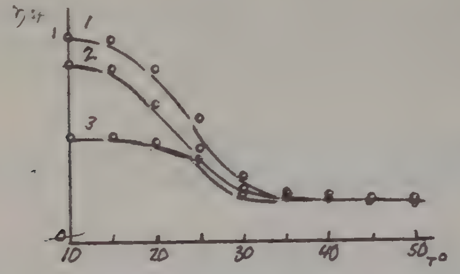

Fig. 7. Specific viscosity of 0.5% solutions of gelatin, prepared: 1 — in water; 2 — in 1 M acetamide solution; and 3 — in 1 M urea solution.

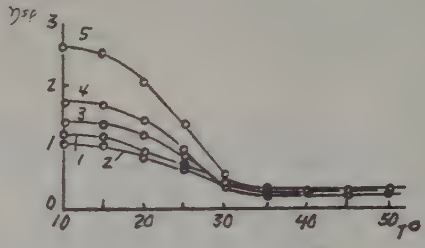

Fig. 8. Specific viscosity of 0.5% solutions of gelatin, prepared: 1 — in water; 2 — in 0.05 M; 3 — in 0.5 M; 4 — in 1 M; 5 — in 2 M glycine solution.

In our study of the mechanical properties of gels we showed that acetamide, which contains a single amino group in its composition, is a less active addition than urea, which has two amino groups.

A similar picture is seen in the study of the viscosity of gelatin solutions. It is seen from Figure 7 that replacement of an amino group by a methyl group weakens the dispersing effect of the addition.

An interesting effect is observed on the addition of aminoacetic acid to 0.5% gelatin solution.

It can be seen from Figure 8 that small amounts of glycine produce a weakening of intermolecular action in 0.5% gelatin solution. However, this effect disppears as the concentration of glycine increases. Further to this, increase in the concentration of this substance in the solution even leads to an increase of viscosity and consequently to an increase of the interaction forces in the system. The cause of the different effects of small and large amounts of glycine on the viscosity of 0.5% solutions of gelatin is insufficiently clear.

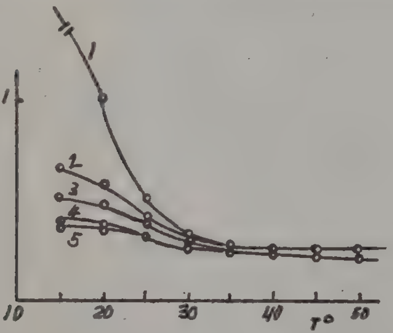

Fig. 9. Effect of quinone on the viscosity of 0.5% gelatin solutions with the following contents of quinone relative to the gelatin: 1 — 0.1%; 2 — 1.0%; 3 — 2.0%; 4 — 3.5%; 5 — 5.0% urea.

Data on the influence of quinone on the viscosity of gelatin solutions are shown in Figure 9. As in the case of gels, the quinone was added in the form of an alcoholic solution.

It follows from the curves of Figure 9 that increase of the quinone concentration produces a lowering of the viscosity of 0.5% solution at low temperatures. Thus, the action of quinone on the viscosity is, formally, the same as that of ammonium nitrate and urea. However, the molecular mechanism of this action is apparently not identical. Indeed, urea and ammonium nitrate, as we have noted already, displace the melting point of the gel in the direction of lower temperatures, while in presence of quinone the gel does not melt at 90-100°. This difference is apparently due to the fact that urea and ammonium nitrate in all cases only weaken the intermolecular and intramolecular bonds, while quinone blocks or eliminates these bonds. As quinone contains two active groups, such blocking in concentrated solutions leads to vulcanization or formation of stable cross-bonds in the gel, while in dilute solutions the blocking takes place mainly within the limits of one or a few molecules. For this reason the gelatin molecules become more hydrophobic and less reactive. All this leads to the result that a tanned solution of gelatin becomes less viscous than an untanned one.

Our experiments on viscosity are in direct agreement with Sokolov's observations [5].

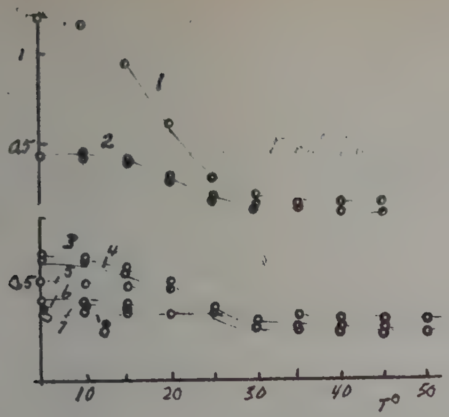

Fig. 10. Effect of formalin and urea on the viscosity of 0.5% gelatin solutions tanned with 5% quinone: 1 — water; 2 — 1 and 2.5% solution of formalin; 3 — water; 4 — 0.1 M; 5 — 0.5 M; 6 — 1 M; 7 — 2 M; 8 — 5 M solutions of urea.

Figure 10 shows our results, from which it is seen that even 1% formalin, like quinone, sharply decreases the solution viscosity.

It must be stressed, however, that quinone does not block all the local bonds. This follows from the fact that urea lowers the viscosity of gelatin solutions even when they have been tanned to the limit, as can be seen from the same Figure 10.

SUMMARY

1. The interaction processes in solutions and gels of gelatin are determined by the formation of local bonds, in the first instance between the polar groups of the gelatin molecules.

2. The greatest effects of the dispersing action or weakening of intermolecular interaction are observed in presence of ammonium nitrate and urea. Ammonium nitrate and urea in large amounts not only decrease the viscosity of dilute gelatin solutions, but sharply lower the temperature of the disintegration of the gel network structure. Alcohols and acetamide are less active additions.

3. Glycerol, barium sulfate, and calcium sulfate have no effect on the interaction processes. Quinone and formalin, when added to the solutions, block the polar groups, which results in a fall of the solution viscosity in the presence of these substances. Aminoacetic acid in small amounts decreases the viscosity of gelatin solutions, but, on the contrary, larger amounts produce a sharp increase of viscosity.

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EFFECT OF ELECTROLYTES OF THE VISCOSITY OF NITROCELLULOSE SOLUTIONS

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It is known that electrolytes added to nonaqueous solutions of nitrocellulose or other cellulose esters may raise or lower the viscosity of such concentrated solutions or may leave it unchanged [1].

The mechanism of the increase of viscosity of cellulose ester solutions by the action of electrolytes has been studied by Papkov [2] in adequate detail, and consists of the formation of spatial structures ("three-dimensional molecules"), in which the electrolytes play the part of "bridge" linkages between the chains. The decrease of viscosity of concentrated solutions of cellulose esters has not yet received a final explanation. The indications available in the literature that electrolytes which cause a lowering of the viscosity of cellulose ester solutions destroy their structure, are too general, while their action in causing degradation of the cellulose esters is not proved experimentally and is improbable [3].

In the most precise of the experimental studies on the action of electrolytes on the viscosity of concentrated solutions of nitrocellulose, Mikhailov and Kargin [4] showed that the explanation of the viscosity decrease is that the electrolyte molecules adsorbed at the active regions of the nitrocellulose chains destroy the structural bonds between the chains, and that the sorption of electrolytes by nitrocellulose in solutions is predominately molecular in nature [4]. However, even in this paper, which undoubtedly gives a correct view of the phenomenon, the quantitative aspect was not investigated, nor was the nature of the active groups of the nitrocellulose chains, which determine structure formation in the solution, and the blocking of which leads to decrease of viscosity.

The present study is devoted to the elucidation of these aspects of the problem.

EXPERIMENTAL

Nitrocellulose with 11.51% nitrogen and 0.17% ash content, acetone, and lithium chloride were used in the experiments. Particular attention was paid to removing water as completely as possible from these materials. The viscosity of 0.2 and 2% solutions of nitrocellulose in acetone was determined in a capillary viscosimeter over a wide range of pressures, so that it was possible to determine not only the total viscosity of the solution, but its structural component. The latter was calculated by the method proposed by Pasynsky and Rabinovich [5], on the basis of the curve for the dependence of the viscosity η on the logarithm of the velocity gradient log G; the velocity gradient was found from the Formula:

$$G = \frac{3Q}{\pi r^3 t} = \frac{k}{t} \ \sec^{-1},$$

where the constant k = 5450.

The viscosity was calculated from the well-known Poiseuille Equation:

$$\eta = \frac{\pi r^4}{8Ql} Pt = CPt.$$

The constant C, the value of which was 0.005, was determined in an experiment with castor oil, which is a normal liquid with a known coefficient of internal friction (η_{20} = 950 centipoises). All the viscosimetric determinations were carried out at 20° ± 0.5° C.

To obtain data concerning the possibility of degradation of nitrocellulose by the action of electrolytes, the molecular weights of nitrocellulose precipitated from the solutions were determined. The molecular weight

TABLE 1

Variations of Viscosity of Nitrocellulose Solutions.

Nitrocellulose	Pressure in mm Hg	Viscosity in centipoises	Nitrocellulose	Pressure in mm Hg	Viscosity in centipoises
Without addition of LiCl	10	17.0	In presence of LiCl in amounts equivalent to the ONO_2 groups of nitrocellulose	10	3.81
	20	15.9		20	3.80
	80	15.5		40	3.83
	128	15.0		50	3.80
	160	14.3		60	3.79
	240	13.0		70	3.81
	300	12.2		80	3.81
In presence of LiCl in amounts equivalent to the OH groups of nitrocellulose	10	13.8	In presence of LiCl in amounts equivalent to the OH and ONO_2 groups of nitrocellulose	10	3.79
	20	12.8		20	3.78
	40	12.5		40	3.80
	80	11.9		50	3.77
	120	11.6		60	3.83
	160	11.4		70	3.81
	240	11.1		80	3.76
	300	11.0			

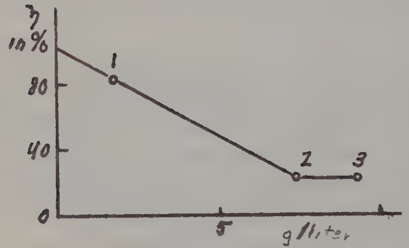

Fig. 1. Relative decrease of the total viscosity of 2% acetone solution of nitrocellulose in presence of different amounts of LiCl: 1) concentration of lithium chloride, equivalent to the OH groups; 2) to the ONO_2 groups; 3) to the OH + ONO_2 groups.

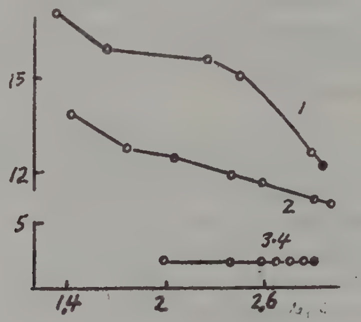

Fig. 2. Dependence of the viscosity of 2% acetone solution of nitrocellulose on the logarithm of the velocity gradient: 1) without LiCl; 2) in presence of LiCl in an amount equivalent to the OH groups; 3) to the ONO_2 groups; 4) to the OH + ONO_2 groups.

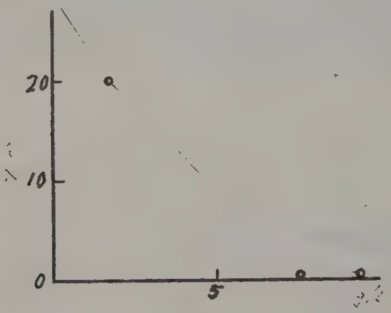

Fig. 3. Variations of the structural viscosity of 2% acetone solution of nitrocellulose as percentages of the total viscosity in presence of different amounts of LiCl: 1) amount of LiCl equivalent to the OH groups; 2) to the ONO_2 groups; 3) to the OH + ONO_2 groups.

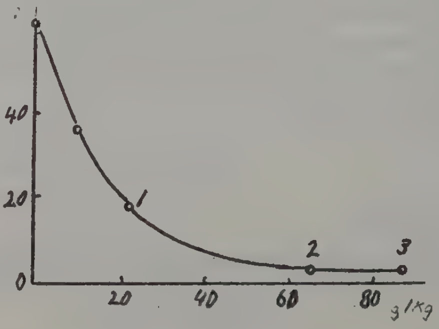

Fig. 4. Dependence of the viscosity of 18% nitrocellulose solution in alcohol-ether mixture on amount of LiCl: 1) amount of LiCl equivalent to the OH groups; 2) to the ONO_2 groups; 3) to the OH + ONO_2 groups.

determinations were based on the specific viscosity of 0.1% solutions of nitrocellulose in acetone; the Staudinger formula [6] was used for the calculations.

Table 1 shows the variations of the viscosity of 2% solutions of nitrocellulose in acetone with different amounts of added lithium chloride.

The total viscosity of nitrocellulose solutions and its variations on addition of LiCl in various concentrations may be compared from the values in Table 1 which correspond to a pressure of 10 mm Hg. A graph for the relative decrease of total viscosity in relation to the total lithium chloride added is plotted (Figure 1), taking the total viscosity of a 2% solution without added lithium chloride at a pressure of 10 mm as 100%. To show the course of changes in the structural viscosity, Figure 2 shows curves for the dependence of viscosity on the logarithm of the velocity gradient.

Structural viscosity, according to Pasynsky and Rabinovich [5], may be quantitatively characterized by the tangents of the angles of inclination of the curves of Figure 2, which are zero for solutions containing lithium chloride in concentrations equivalent to the ONO_2 and OH + ONO_2 groups; for a nitrocellulose solution without lithium chloride, the tangent of the angle is equal to 1.087, while for a solution with lithium chloride added in an amount equivalent to the OH groups it is equal to 0.325.

From a comparison of the viscosity values measured at maximum and minimum pressures, η_{max} and η_{min} (Table 1) it is possible to show the role of the structural component in the total viscosity of solutions containing lithium chloride in different amounts, as is shown in the curve of Figure 3.

It is clear from the results shown that as the electrolyte concentration increases, the total and structural viscosities decrease until the electrolyte concentration reaches a value molecularly equivalent to the ONO_2 groups in the nitrocellulose; the total viscosity of the solution reaches a minimum value which remains unaltered on further increase of the concentration of lithium chloride, while the structural viscosity becomes zero.

A study of 18% solutions of nitrocellulose in alcohol-ether mixture showed an analogous relation between the decrease of viscosity and the amount of added electrolyte. Figure 4 shows a curve for the dependence of the total viscosity on the amount of lithium chloride added to a concentrated (18%) solution of nitrocellulose. The values of the molecular weight of the nitrocellulose precipitated from the solutions are shown in Table 2.

TABLE 2

Molecular Weight of Nitrocellulose Precipitated from Solutions.

Nitrocellulose	Specific viscosity	Molecular weight
Precipitated from solution without added LiCl	0.140	43590
Precipitated from solution with LiCl in an amount equivalent to OH groups	0.136	42350
Precipitated from solution with LiCl in an amount equivalent to the ONO_2 groups	0.143	44520
Precipitated from solution with LiCl in an amount equivalent to the OH + ONO_2 groups.	0.138	42970

As is seen from the data of Table 2, the molecular weight of nitrocellulose remains essentially unchanged by the addition of electrolyte, and therefore the electrolyte has no depolymerizing effect on nitrocellulose.

DISCUSSION

The fact that the molecular weight of nitrocellulose is not lowered in presence of electrolyte clearly proves that no degradation of the nitrocellulose takes place, and the decrease of viscosity is due to other causes. Thus, Drinberg's supposition [3] concerning the depolymerizing action of electrolytes is incorrect. At the same time, the well-defined course of the decrease of structural viscosity of nitrocellulose solutions, which is proportional to the concentration of electrolyte until the structural bonds between the active groups of the high polymer are destroyed, shows that the decrease of viscosity of nitrocellulose solutions on addition of electrolyte is in all probability the result of sorption of molecules of the latter on the active groups of nitrocellulose. The sorption of electrolyte results in rupture of the structural bonds in nitrocellulose solutions, and, consequently, in a decrease of the structural viscosity. Examination of the experimental data shows also that the active groups of nitrocellulose, which produce structure formation as a result of their interaction in solution, are only the ONO_2 groups, and the OH groups have no relation to structure formation in solution. The fact that electrolytes affect only the structural component of the viscosity is confirmed because in dilute solutions of nitrocellulose (0.2%), in which anomalous viscosity is absent, electrolytes do not cause a change of viscosity.

SUMMARY

The effect of LiCl on structure formation in solutions of nitrocellulose in acetone and alcohol-ether mixture was studied.

1. It is shown that LiCl does not cause depolymerization of nitrocellulose in solution. Dilute solutions of nitrocellulose, which do not have structural viscosity, do not change their viscosity on addition of this electrolyte.

2. In concentrated solutions of nitrocellulose, addition of LiCl lowers only the structural component of viscosity. The supposition is put forward that the mechanism of the action of LiCl consists of its sorption on the ONO_2 groups of nitrocellulose, the result of which is a destruction of the structural bonds between the cellulose ester chains in solution.

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INVESTIGATION OF THE STRUCTURE OF SYNTHETIC POLYAMIDE FIBERS

III. DIFFERENTIAL HEATS OF SORPTION OF WATER BY CAPRON FIBER

N. V. Mikhailov and E. Z. Fainberg

In the preceding communications [1, 2], the results of measurements of the sorption of water and the integral heats of wetting of capron fiber by water are given. These studies showed the effect of physical structure of capron fiber on its heat of wetting and sorption of water. Examination of the results of measurements of sorption and integral heats of wetting led us to the supposition that the peculiarities of sorptional behavior of capron fibers of different physical structure are determined by differences in the energy of bonding between polycaprolactam molecules and water. However, for a deeper study of this question, it is also necessary to investigate the differential heat of sorption of water by capron fiber. The present paper is devoted to a study of the differential heats of sorption of water by capron fibers of different physical structure.

As was already indicated earlier [2], the integral heats of wetting of synthetic fibers, and in particular, of polyamide fibers, have not been determined up to the present. The differential heats of sorption of polyamide fibers have also never been determined, as their measurement presents still greater experimental difficulties. There is only a small number of papers in which the authors attempt to find the heat of sorption of water by polyamides from calculations of the sorptional equation constant [3], or from calculations of the isosteric heats of sorption.

It should be noted, however, that when the heat of sorption is calculated from the sorptional equation [3]

$$c = \frac{a_1 b_2}{a_2 b_1} e^{\frac{E_1 - E_L}{RT}}$$

it is assumed that the ratio $\frac{a_1 b_2}{a_2 b_1}$ is close to unity. Here, as is known, a_1, a_2, b_1, b_2, are constants associated with the formation and evaporation of the first and subsequent layers of the adsorbed molecules. However, as the data of the paper [4] show, $\frac{a_1 b_2}{a_2 b_1}$ is not equal to unity, but may vary within very wide limits. Therefore, the use of this equation requires the empirical determination of the constants a_1, a_2, b_1, b_2 in each instance, which is sometimes associated with assumptions having little basis. Thus, calculation of the heat of sorption from the equation [3] cannot give completely reliable results. In calculations of the isosteric heat of sorption the basic assumption is that the thermal effect of sorption is independent of the temperature, which is not found in fact.

Because of the small temperature coefficient of sorption of water by capron fiber, small errors in the measurements must significantly distort the results, which substantially limits the applicability of this method.

In this study, the values of the differential heats of sorption are calculated from experimentally determined integral heats of wetting by water of capron fibers of different moisture contents.

As is known, the relationship between the integral and the differential heat of sorption is of the form:

$$\frac{dW}{dc} = Q_s,$$

where W is the integral heat of wetting; Q_s is the differential heat of sorption; c is the amount of moisture sorbed by the fiber.

Capron fibers prepared at the same time were used in all the measurements. The preliminary treatment of the specimen was similar to that described in the previous paper [2], in which the dependence of the heat of wetting on the "age" of the fiber was demonstrated. To eliminate the effect of "age" of the fiber on its heat of wetting by water, both the oriented and nonoriented fibers were stored for a time sufficient to attain a constant value for the heat of wetting.

The fibers were conditioned on the sorption apparatus in the following way: four ampoules were simultaneously filled with air-dry fiber; the amount of fiber placed in each ampoule was determined by weighing; all the four ampoules were fused to a "comb" connected to the sorption apparatus described previously. At the same time as the specimens were placed in the ampoules, a weighed sample of the air-dry fiber was suspended from a tungsten spring contained in the sorption tube, and dried in a vacuum to constant weight.

The end of the drying process was determined from constancy of the cathetometer readings. When the dry state was reached, a definite amount of water vapor was introduced into the sorption system. The attainment of the equilibrium state was again determined from the constant cathetometer readings. The amount of moisture in the fiber was calculated from the extension of the spring of the sorption balance. The calculation could also be made from the sorption isotherm for the given fiber. It should be noted that, as a check experiment showed, the difference between the moisture contents determined by these two methods did not exceed the limits of experimental error. The amount of moisture absorbed by the fiber can, in our conditions, be determined to an accuracy of ± 0.06%. The heat of wetting of the fiber by water was determined with the calorimetric apparatus described previously [2].

RESULTS OF THE DETERMINATIONS, AND DISCUSSION

Figures 1 and 2 show the results of measurements of the integral heat of wetting of nonoriented and oriented fiber for various water contents. The squares on the curves represent the regions of the determination errors, both calorimetric (ordinate axis), accuracy of measurement ± 0.1 cal., and sorptional, (abscissa axis), accuracy of measurement ± 0.06%.

The values of the differential heats of sorption, calculated from the tangent of the slope of the curves in Figures 1 and 2 to the abscissa axis, are shown in Figure 3*.

As Figures 1 and 2 show, the curves showing the dependence of the integral heat of wetting of capron fiber on its moisture content consist, within the limits of experimental error, of two linear regions. The points of inflexion in the curves are different for the nonoriented and oriented fibers. While the point of inflexion for the nonoriented fiber is at 2.60%, it is at 1.50% moisture content for oriented fiber.

Extrapolation of Curves 1 and 2 to the abscissa axis shows that the thermal effect of wetting should be zero when the moisture content of nonoriented fiber is 7.10%, and that of oriented fiber, 6.04%. This amount of moisture is in fact sorbed by these fibers at a relative vapor pressure of water vapor $P/P_0 = 0.75$-0.80. According to our latest results, when $P/P_0 = 1$, nonoriented fiber absorbs 13% water, and oriented, 8%.

Thus, the sorption of water vapor from 7.1 to 13% by nonoriented fiber, and from 6 to 8% by oriented fiber, proceeds with a zero thermal effect of wetting, and the heat of sorption corresponds to the heat of condensation of water. Further sorption is apparently associated with the formation of polylayers or with commencement of capillary condensation.

To the best of our knowledge, the existence of two constant values of differential heats of sorption in polymers has not been observed. An analogous fact was established in work with silicic acid gels [5], although these results are open to doubt [6]. Irrespective of whether the differential heat of sorption for silicic acid gels is constant, explanations of that fact cannot be used in the case of polyamides, as the gels of silicic acid used were amorphous, and synthetic polyamide is a crystalline substance. In addition, one cannot ignore differences in the molecular structure of these substances, in particular in view of the supposition put forward by one of us [7, 8] of the possible existence of cyclic compounds within the polycaprolactam macromolecules, due to intramolecular hydrogen bonds.

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*On the experimental curve which shows the dependence of the heat of wetting on the amount of previously adsorbed water vapor, the differential heat of wetting, or the heat of sorption from the vapor state, is determined direct if the value q of the latent heat of condensation of the vapor is taken into account. As the value of q is constant, it is omitted from the calculations, which should not change the character of the curve or change the interpretation of the experimental results.

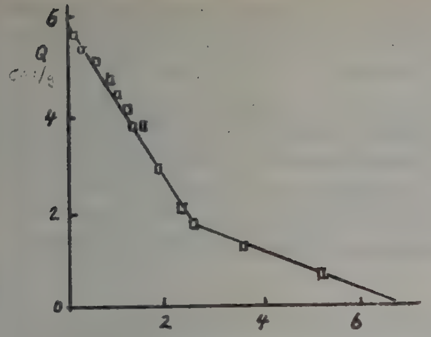

Fig. 1. Dependence of the integral heat of wetting (Q) of nonoriented capron fiber on the moisture content.

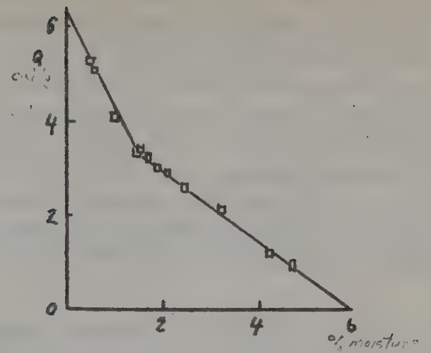

Fig. 2. Dependence of the integral heat of wetting (Q) of oriented capron fiber on the moisture content.

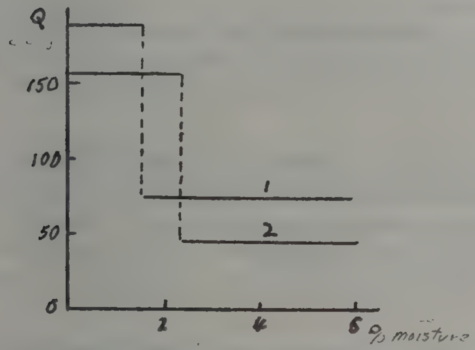

Fig. 3. Differential heat of sorption of water: 1) by oriented, and 2) by nonoriented capron fiber.

The values of the differential heats of sorption by oriented and nonoriented fibers may be interpreted on the basis of the accepted views of the nature of sorptional processes in synthetic polyamides and in polymers generally.

For example, in some foreign papers [9, 10] attempts are made to approach an evaluation of results on isosteric heats of sorption of water by nylon on the basis of the polymolecular sorption theory [3], by calculation of the number of sorptional layers which corresponds to definite values of the heat of sorption of water. Another approach is made on the assumption of the existence of amorphous and crystalline regions in polyamides; this, for example, is done by Hermans in the case of hydrate cellulose fibers. Usmanov and Kargin [11] explain differences in the sorption capacity of hydrate cellulose fibers by the influence of the packing density of the polymer molecules.

In discussion of the experimental results we make the primary assumption that the predominant part of the sorbed water must be related to the carbamide groups, while, for an average molecular weight of 10,000, the end groups, even if they are completely accessible to the diffusion of water molecules, should take only a small part of the sorbed water, say approximately 2%.

Consequently, even the initial values for the sorption of water, both 1.5% for oriented fiber and 2.6% for nonoriented fiber, which correspond to the maximum value of the differential heat of sorption, greatly exceed the calculated values for the end groups, and therefore such a value of the differential heat cannot be explained by sorption of water by the end groups in polycaprolactam.

A simple stoichiometric calculation shows that 15% of water is needed for a single monomolecular coating of the CONH groups in the whole volume, which is more than the total amount of absorbed water. It must, therefore, be assumed that the sorption proceeds not in the whole volume, but only in part of it. The assumption of the formation of polylayers not in the whole volume, but only in a part of it is not without basis, but is improbable in view of the very small values of the secondary thermal effect, which differs very slightly from the value of the heat of condensation of water.

That considerable portion of the absorbed water, the heat of sorption of which corresponds to the heat of condensation of water, cannot affect the value of the differential heat of sorption. In our view a more probable explanation of the nature of the differential heats of wetting may be obtained on the basis of an assumption of the existence of two types of hydrogen bonds in caprolactam: intra- and intermolecular hydrogen bonds.

It is quite probable that our results may be explained with a concept of a different nature of water sorption, for example, sorption in the micropores of the material or sorption which proceeds by a diffusion mechanism.

However, in absence of direct data on change of volume of the specimen during sorption of water, we cannot use these concepts to explain the mechanism of sorption. Comparison of the curves of Figure 3 shows that the points of inflexion of the differential heats of sorption are different for nonoriented and oriented fibers; for nonoriented fiber the inflexion point represents 2.6% of sorbed water, while for oriented fiber, it is 1.5%. The different amounts of sorbed water corresponding to the points of inflexion are to be explained, in our view, by the fact that the first branch of the curve relates to the bonding of water by intramolecular hydrogen bonds in the cyclic regions of the polycaprolactam molecule, and the second, by intermolecular bonds. The decrease in the amount of sorbed water from 2.6 to 1.5% on passing from nonoriented to oriented fiber should be explained on the view that in the process of fiber orientation intramolecular hydrogen bonds are converted into intermolecular by deformation or straightening of the cyclic regions during stretching. This viewpoint is in good agreement with the experimental data.

It follows from these views that intramolecular hydrogen bonds should be less stable than the intermolecular, although for a final solution of this question, it is necessary to carry out additional investigations with the use of methods which permit direct identification of these bonds.

It should be taken into account that polymers cannot form crystals of macroscopic dimensions, and a certain portion must remain in a state of disturbed structure, where regions with intramolecular hydrogen bonds have the greatest probability of formation.

Therefore, a change in the ratio of intermolecular and intramolecular hydrogen bonds is entirely probable in changes of polycaprolactam structure. This gives a basis for the supposition that the relationship between the points of inflexion on the curves for the differential heats of wetting of oriented and nonoriented fiber may serve as a measure of changes in the defectiveness of the crystalline structure of polycaprolactam during the transition from nonoriented to oriented fiber.

It appeared of interest to evaluate the total value of the thermal effects of sorption for all the regions of the curve for the differential heat of sorption; that is, to calculate the area under the differential heat of sorption curves. It was found that in both cases, the total differential heat of sorption was the same, 600 calories. The agreement between the values of the total differential heats of sorption of oriented and nonoriented fibers, with different amounts of sorbed water, is evidence that the formation of polylayers, even if it occurs, has very little or no influence on the nature of the differential heat of wetting.

Support is therefore given to the viewpoint that the values of the differential heat of sorption of water by polycaprolactam are essentially determined by structural peculiarities, and not by the formation of polylayers. The cause of the deviation between the values of the differential heats of wetting of oriented and nonoriented fiber is still not clear.

SUMMARY

1. Measurements were made of the integral heats of wetting of nonoriented and oriented capron fibers by water in relation to their moisture contents.

2. The differential heats of sorption of water by polycaprolactam were calculated and it is shown that there are two constant values for these, corresponding to different regions of the sorption isotherm.

3. The nature of the inflexions on the curves for the differential heats of sorption is in agreement with the view previously advanced concerning the existence of different types of hydrogen bonds in polycaprolactam — intra- and intermolecular — changes in the ratio of which during orientation of the fiber is the cause of displacement of the inflexion points on the curves for the differential heats of wetting.

4. The relationship between the inflexion points on the differential heat of sorption curves for oriented and nonoriented capron fibers may serve as a measure of the defectiveness of the crystalline structure of polycaprolactam.

5. The total values of the differential heat of sorption, obtained by calculation of the areas under the curves, are in good agreement with the data of other authors on the absence of differences in the crystal lattice parameters of oriented and nonoriented capron fibers.

In conclusion, we express our gratitude to Doctor of Chemical Sciences, S. M. Skuratov for valuable advice on the thermochemical measurements, and also to laboratory assistants, T. I. Karetina and Z. N. Zaspinok for help in preparing, drying, and conditioning the specimens.

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EFFECT OF STRUCTURIZING AGENTS ON THE PLASTICIZATION AND VULCANIZATION OF BUTADIENE-STYRENE RUBBER

A. S. Novikov and F. A. Galil-Ogly

It is now established that in the plasticization and vulcanization of butadiene-styrene rubber structure formation and destruction processes occur simultaneously [1]. It is of interest both from the practical and theoretical points of view to seek methods for regulating the destruction and structure formation processes in the plasticization and vulcanization of rubbers, which would provide possibilities for control of the kinetics of these processes and of the physico-chemical properties of rubbers and vulcanizates. In this connection, the most effective substances in vulcanization might be those which either retard the destructive processes, or direct oxidative processes to structure formation, and, in plasticization, direct them to cause destruction.

It is known from the literature [2] that various organic compounds (anisidine, benzidine, aminophenols, nitroso compounds, etc.) have a structurizing effect on natural rubber, which is manifested in a decrease of plasticity and an increase of viscosity of rubber solutions. There is no doubt that these substances also have an effect in destruction and structure formation processes which occur in the plasticization and vulcanization of synthetic rubber.

We undertook a study of the effect of a series of substances of the types indicated on the properties of butadiene-styrene rubber during plasticization and vulcanization.

EXPERIMENTAL

The structurizing agents initially studied were p-anisidine, benzidine, 1,4-diphenyl phenylenediamine, and benzoquinone, and a later detailed study was made only of p-anisidine and 1,4-diphenyl phenylenediamine, which were the most effective*.

The material selected for study was butadiene-styrene rubber SKS-30A, which does not crystallize on stretching and at the same time yields a relatively strong rubber without active fillers.

The effect of the named substances on the properties of raw SKS-30A rubber was studied by changes in the viscosity of 0.5% solutions in toluene on heating (determined in an Ostwald viscosimeter for volatile liquids at a temperature of 25° ± 0.1), solubility, plasticity, rate of mechanical and thermo-oxidative plasticization, and also by values of the induction period of oxidation.

It follows from the results shown in Figure 1 that addition of structurizing agents to solutions of SKS-30A rubber produces an increase of relative viscosity, which increases with increase of heating time at 80°.

The effects of 1,4-DPPD and PA on changes of relative viscosity when the rubber solutions are heated are not the same: in the case of 1,4-DPPD added in amounts of 0.3 and 1.0% of the rubber, the relative viscosity rises steadily with increased time of heating, while the addition of PA in the same amounts first produces some lowering of the relative viscosity, and then an increase.

This effect of 1,4-DPPD and PA on solutions of SKS-30A rubber may be explained by the fact that the first is a powerful, and the second a weak inhibitor of rubber oxidation. The weaker inhibiting action of PA, in comparison with 1,4-DPPD, is confirmed by a shorter induction period in the oxidation** of sodium butadiene rubber without added antioxidant.

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* The following abbreviations are used in the text: PA — p-anisidine; 1,4-DPPD — diphenyl phenylenediamine; MBT — mercaptobenzothiazole.

** The oxidation was carried out in film form at 120°, with Nekrasov apparatus.

In the case of technical SKS-30A rubber, containing 2.1% of Neozone D, subsequent addition of p-anisidine in an amount of 0.5 parts by weight per 100 parts by weight of the rubber does not alter the induction period of oxidation at 130° (Table 1).

The rate of thermal plasticization* of SKS-30A was decreased considerably in presence both of 1,4-DPPD and of PA (Figure 2). While in the case of 1,4-DPPD this may be due to inhibition of oxidative processes which occur in the rubber during thermal plasticization, in the case of PA it may be due to a specific structurizing effect of the latter on the rubber during thermal oxidation. Only an insignificant decrease in the rate of the process was found in cold plasticization on rollers.

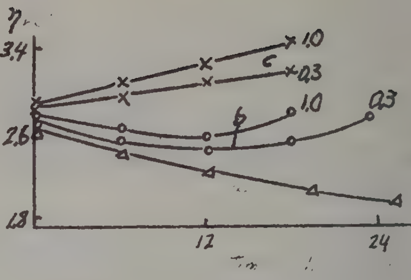

Fig. 1. Variation of the relative viscosity of 0.5% solution of SKS-30A in toluene on heating at 80°; a) without addition; b) PA; c) 1,4-DPPD.

In presence of mercaptobenzothiazole the plasticization process of SKS-30A rubber is accelerated, as was shown earlier by Karmin and Bets [3] for SKS-30 rubber. A notable feature is the considerable intensification of structure formation in the rubber during thermal plasticization in the simultaneous presence of MBT and PA or 1,4-DPPD, as shown by the loss of solubility of the rubber (Figure 3).

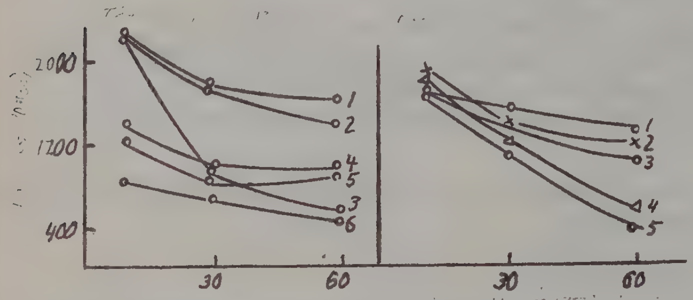

Fig. 2. Variation of plasticity of SKS-30A during mechanical and thermal plasticization in presence of various substances: 1) PA; 2) 1,4-DPPD; 3) without additions; 4) 1,4-DPPD and MBT; 5) PA and MBT; 6) MBT.

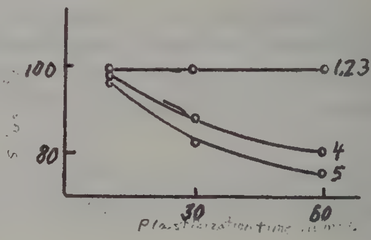

Fig. 3. Change of solubility of SKS-30A on thermal plasticization in presence of various substances: 1) without additions; 2) PA (0.5); 3) 1,4-DPPD (0.5); 4) MBT and PA (1.0 and 0.5); 5) MBT and 1,4-DPPD (1.0 and 0.5).

TABLE 1

Value of the Induction Period of Oxidation of SKB and SKS-30A in Presence of p-Anisidine and 1,4-Diphenyl Phenylenediamine

Rubber	Oxidation temperature (°C)	Amount added, parts by wt. per 100 parts by wt. of rubber			Induction period, min.
		Neozone D	PA	1,4-DPPD	
SKS-30A.	130	2.1	—	—	120
	130	2.1	0.5	—	120
SKB	120	—	—	—	30
	120	—	0.5	—	60
	120	0.5	—	—	210
	120	0.5	0.5	—	240
	120	—	—	0.5	300

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*The thermal plasticization of the rubber was carried out in an autoclave at 130° under an air pressure of 3 atm.

The plasticity of rubber thermally plasticized in presence of PA or 1,4-DPPD, is considerable lower than that of rubber thermally plasticized in the simultaneous presence of MBT and PA, and also of MBT and 1,4-DPPD. However, the thermally plasticized products obtained in presence of PA and 1,4-DPPD, are fully soluble, while those obtained in the simultaneous presence of MBT and PA, and also of MBT and 1,4-DPPD are only partially soluble, which is direct proof of the structurization of the rubber.

Thus, the same structural changes are observed, accompanied by increased plasticity of the rubber and partial loss of solubility, in the simultaneous presence of MBT and the studied structure-forming substances during thermal placticization.

Therefore, in the thermal plasticization of SKS-30A in presence of MBT, 1,4-DPPD and PA do not act as a strong and a weak inhibitor of rubber oxidation, but a different mechanism operates, which is due to the combined action of MBT and these substances, which finally leads to the same structural changes.

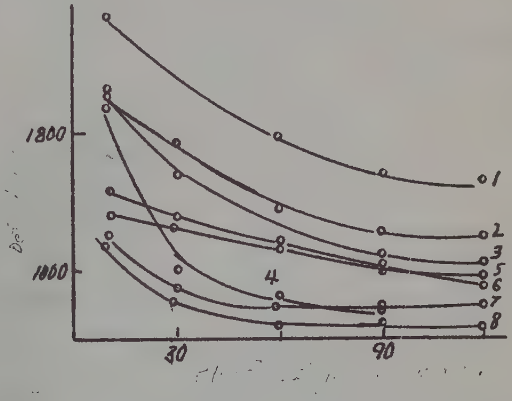

Fig. 4. Defoe hardness of SKS-30A in presence of various substances: 1) PA; 2) 1,4-DPPD and PA; 3) 1,4-DPPD; 4) without additions; 5) benzothiazole-2-sulfenediethylamide and PA; 6) MBT and PA; 7) benzothiazole-2- sulfenediethylamide; 8) MBT.

It should be noted that structure formation under the influence of PA and 1,4-DPPD during thermal plasticization, with simultaneous loss of solubility, is observed only in presence of MBT accelerator. The use of the vulcanization accelerator benzothiazole-2-sulfenediethylamide together with PA and 1,4-DPPD gives thermal plasticization products with a plasticity equal to that of products obtained by the simultaneous action of PA and MBT, but they retain complete solubility (Figure 4).

Complete solubility is also retained by thermal plasticization products obtained by the simultaneous action of PA or 1,4-DPPD with diphenylguanidine, although the plasticity of these is considerably less than that of the products obtained with MBT and PA.

Thus, the same structural changes, accompanied by decrease of plasticity, are observed in the simultaneous presence in SKS-30A rubber of PA or 1,4-DPPD and vulcanization accelerators (benzothiazole-2- sulfenediethylamide or MBT) during thermal plasticization.

However, the extent of the structural transformations during thermal plasticization of the rubber, in the present case the increase of spatial structure, is different in the simultaneous action of PA or 1,4-DPPD and the above accelerators, as is shown by the differences in the solubility of the rubber after plasticization.

The effect of structurizing substances on the physico-mechanical properties of unfilled vulcanizates and vulcanizates, filled with channel black was studied with the following compositions, in parts by weight:

	Composition 1	Composition 2
Rubber	100.0	100.0
Stearin	2.0	2.0
Zinc white	5.0	5.0
Mercaptobenzothiazole	2.0	2.0
Channel black	—	30.0
Sulfur	2.0	2.0
Structurizing agents	1.0	1.0

The mixtures were prepared on 150 x 300 mm laboratory rollers, using a mechanical and a thermal plasticization product of SKS-30A with equal Defoe hardness, of 1000 g. The procedure for adding the ingredients was the same in both cases, with the exception of the structurizing addition.

It will be shown later that the order in which the structurizing substances are added to the rubber, by mixing with the ingredients or adding to the rubber during plasticization, has a significant effect both on the properties of the mixture and on the physico-mechanical properties of the vulcanizates if a mechanically plasticized product is used.

TABLE 2

Physico-Mechanical Properties of Unfilled and Filled Vulcanizates of SKS-30A, Containing Structurizing Additions.

Formulation of mixture and product type	Structurizing agents and amounts	Order of addition of structurizing agents	Vulcanization at 143°, min.	Modulus in kg/cm^3 at 300%	Tensile limit kg/cm^2	Relative elongation, %	Residual elongation, %	Rebound elasticity
Thermal plasticization								
Composition 1	PA 1.0	To rubber during mixture	20	21	37	450	5	54
	—	—	40	11	20	440	13	53
	1,4-DPPD 1.0	To rubber during mixture	20	23	41	530	10	—
Composition 2	PA 1.0	"	20	63	204	620	20	50
	1,4-DPPD 1.0	"	20	59	189	586	11	51
	—	—	80	55	100	490	20	49
	PA 1.0	To rubber during thermal plasticization . . .	20	61	222	600	10	—
Mech. plasticization								
Composition 1	PA 1.0	To rubber during mixture	20	11	22	574	6	—
	—	—	20	8.8	18	540	10	—
Composition 2	PA 1.0	To rubber during mixture	40	49	160	680	12	49
	—	—	60	46	134	720	18	48
	PA 1.0	To rubber during plasticization . .	20	52	236	692	19	48

The vulcanizates from thermally plasticized SKS-30A rubber, prepared according to the formulations 1 and 2, irrespective of the order in which the structurizing agents are added, show a certain acceleration of vulcanization together with an increase of tensile strength, equilibrium modulus, and rebound elasticity, while retaining high values of relative elongation (Table 2).

The increase of the limit of accuracy is shown more clearly by vulcanizates prepared according to formulation 2.

The equilibrium modulus was determined by the technique developed by Bartenev [4] with a dynamometer designed by the Mendeleev All-Union Chemical Society. The strength was determined with a Schopper dynamometer at a speed of 500 mm/min., and the rebound elasticity with a pendulum impact apparatus. The test specimens were prepared from 1 mm vulcanized plates by stamping out with a cutter, and were of the shape of a double-ended spade.

Figure 2 shows data on variation of the kinetics of sulfur bonding, and of the equilibrium modulus, in the vulcanization of unfilled mixtures (Composition 1) from thermally plasticized SKS-30A. In presence of PA and 1,4-DPPD the sulfur binding process is slightly accelerated at the start of vulcanization. However, the total amount of combined sulfur does not increase when the vulcanization optimum is reached in presence of PA and 1,4-DPPD.

At the same time, the equilibrium modulus increases considerably, to an equal extent both for the mixture with PA and the mixture with 1,4-DPPD. This indicates the formation of additional chemical bonds in the vulcanizate, which are formed as the consequence of a specific action of PA and 1,4-DPPD on the rubber. In order to confirm the chemical nature of the newly formed bonds, measurements were made of changes in the equilibrium modulus during fatigue of vulcanizates containing PA in comparison with vulcanizates without additions.

The fatigue tests were carried out on Gul's apparatus with periodic extension deformation of 150% amplitude and a frequency of 256 cycles per minute [5].

Figure 6 shows changes of the equilibrium modulus during fatigue of vulcanizates, and it is seen that the nature of these changes is the same for vulcanizates with PA and without it, which indicates that the newly-formed bonds have reasonable stability, as least comparable with that of the sulfur bonds.

In the case of the product of mechanical plasticization, when the structure-forming additions were introduced into the rubber during mixing of the ingredients on the rollers, an increase of the limiting tensile strength of the vulcanizates was not found at all in mixtures prepared according to Composition 1, and it was very slight in mixtures prepared according to Composition 2.

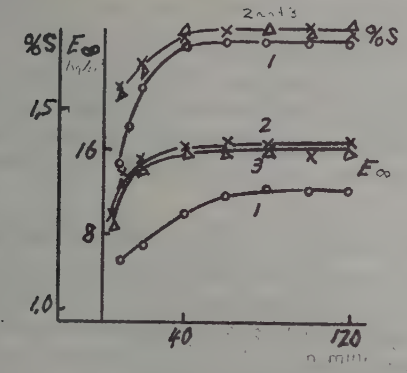

Fig. 5. Kinetics of vulcanization of SKS-30A mixture from changes of E_∞ and combined sulfur: 1) without additions; 2) 1,4-DPPD; 3) PA

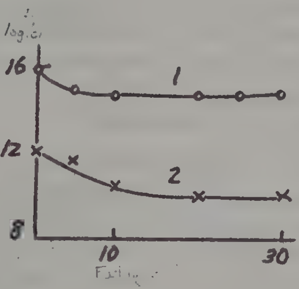

Fig. 6. Changes of the equilibrium modulus of rubbers during fatigue: 1) without additions; 2) PA

By changing the order in which the structurizing substances are added it is possible to obtain an increase of strength in the mechanically plasticized product. If PA is added to the rubber while it is being plasticized on the rollers, and the mixture and vulcanizate are then prepared based on this product, the vulcanizate has higher tensile strength, especially for mixtures prepared according to Composition 2. This indicates that the specific action of the structurizing additions studied is directly related to the oxidative processes which occur in rubber during thermal plasticization and vulcanization.

DISCUSSION

An examination of the experimental results clearly shows the effect of PA and 1,4-DPPD in presence of MBT and other vulcanization accelerators on structural changes which take place both in raw SKS-30A rubber and during its vulcanization.

It is noteworthy that structural changes during vulcanization which are accompanied by an increase in the strength of the vulcanizates are seen most clearly only in thermally plasticized rubber, and are not found in the mechanically plasticized product when the usual sequence of addition of the structurizing substances to the rubber during mixing on rollers is followed.

It may be supposed on the basis of this fact, and also because of the observed viscosity of toluene solutions of the rubber on addition of PA and 1,4-DPPD, that the structural changes which take place in SKS-30A rubber are directly related to the course of oxidative processes, and are due to the reaction of the additions with oxidized regions of the molecular chains, which contain peroxides and other functional oxygen-containing groups or products of their decomposition. Untreated technical SKS-30A rubber, and particularly the thermally plasticized product, may contain considerable amounts of stable peroxides, functional oxygen-containing groups, etc.

Vulcanization accelerators have a considerable influence on the kinetics of the process and on the extent of structural changes in SKS-30A rubber in presence of PA and 1,4-DPPD.

In presence of MBT, which considerably accelerates oxidative processes in rubber, structure formation takes place to the greatest extent in presence of PA and 1,4-DPPD, as is shown by a decrease of the solubility of the rubber on thermal plasticization, and a considerable increase of tensile strength on vulcanization. In this case, there is no difference between the activity and nature of the effect of PA, which is a weak inhibitor of rubber oxidation, and 1,4-DPPD, which is a powerful inhibitor.

Direct structure formation, which results in the joining of separate molecular chains into larger formations or into a spatial network, evidently depends on the concentration of oxidized regions of the molecular chains. This conclusion follows from experimental data on the increase of viscosity of toluene solutions on heating in presence of PA and 1,4-DPPD, and the decrease of the solubility of the rubber on thermal plasticization in presence of these substances with MBT which, by activating oxidative processes, ensures a more rapid accumulation of peroxide radicals in the rubber and accelerates the decomposition of stable peroxides. It should be noted that the specific effect of the additions tested on the mechanical strength of the vulcanizates may be attained in the mechanically plasticized product, if the plasticization of the rubber takes place on rollers in presence of the additions.

Evidently, plasticization on cold rollers does not result in an accumulation of considerable amounts of stable peroxides or other reactive oxidized regions of the molecular chains in the rubber, and therefore the structurizing additions added to the cold plasticized product do not have an effect when the mixture is prepared on the rollers.

When the plasticization takes place on the rollers in presence of the structurizing additions, evidently the rate of reaction of these with the oxidized regions of the molecular chains becomes comparable with the rate of their transformation or decomposition. Under these conditions the additions show a specific effect on the mechanically plasticized product, accompanied by an increase of hardness of the rubber and also an improvement in the physico-chemical properties of the vulcanizates.

Apparently, in addition to structure formation by means of sulfur, the vulcanization process is also accompanied by structure formation caused by interaction between the accelerator, the structurizing addition, and the oxidized regions of the rubber, which leads to the formation of supplementary stable chemical cross-bonds in the vulcanizate, which is confirmed by the higher value of the equilibrium modulus for vulcanizates with structurizing additions as compared with sulfur vulcanizates without additions. The possibility is not excluded that the structurizing additions, by joint action with accelerators, affect the type and nature of the sulfur bonds formed.

In both cases an increase in the number of cross-bonds may take place with an equal amount of combined sulfur. Independently of the reaction mechanism, the vulcanizate structure becomes more complex both as regards the nature of the chemical bonds, and their disposition in the spatial network.

A different disposition of the bonds formed in the vulcanizate in presence of PA and 1,4-DPPD from those formed in the reaction of rubber with sulfur is probably the reason for the retention of high values of relative elongation and the increase of the mechanical strength of vulcanizates, which is shown to the greatest extent in carbon black vulcanizates. As is known, 1,4-DPPD is an effective antifatigue agent for rubbers. Its action was previously explained by the fact that it is a powerful inhibitor of rubber oxidation. It follows from these results that its action in vulcanization is more complex, and is associated with a considerable change of the structure and type of the chemical bonds in the vulcanizate, which may be one of the causes which increase the resistance of the rubber to dynamic fatigue.

SUMMARY

1. Compounds of the type of p-anisidine and 1,4-diphenyl phenylenediamine produce structural changes in SKS-30A rubber and its solutions, especially on heating.

2. Vulcanization accelerators, especially mercaptobenzothiazole, considerably accelerate the structural changes in rubber in presence of p-anisidine and 1,4-diphenyl phenylenediamine both during thermo-oxidative plasticization and vulcanization. The degree and nature of the structural changes in the rubber are different, depending on the type of accelerator.

3. The structurizing effect of p-anisidine and 1,4-diphenyl phenylenediamine in vulcanization is manifested by an increase of mechanical strength, equilibrium modulus, and elasticity of the vulcanizates together with a retention of high relative elongations. The additions somewhat accelerate the addition of sulfur to rubber in the initial stage of vulcanization without increasing the content of bound sulfur at the optimum of vulcanization.

4. The view is put forward that the action of p-anisidine and 1,4-diphenyl phenylenediamine on the observed structural changes in SKS-30A rubber during thermal plasticization and vulcanization are directly associated with the course of oxidative processes, and may be due to interaction of these substances with the oxidized regions of the rubber (peroxide radicals, stable peroxides, functional oxygen-containing groups, etc.) which results in a loss of plasticity and solubility in raw rubber, and, during vulcanization, to formation of supplementary cross-bonds and an increase of strength while high relative elongations are retained. Vulcanization accelerators of the mercaptobenzothiazole type, which activate the oxidative processes in rubber, considerably increase the rate and extent of the structural changes.

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HYDROPHILY OF BENTONITES IN RELATION TO THEIR PHYSICOCHEMICAL NATURE

F. D. Ovcharenko and S. F. Bykov

The wide utilization of bentonite clays in different branches of industry requires exhaustive study of their physicochemical properties. In this connection, we have studied the chemical and mineralogical composition, cation exchange capacity, hydrophily, sorptional properties, and structure of the most economically important bentonite clays of the Georgian and Ukrainian SSR, and established a correlational dependence between these properties.

The materials studied were gumbrin and askangel bentonite clays, kindly supplied by Active Member Acad. Sciences, Georgian SSR, A. A. Tvalchrelidze, and also Ukrainian bentonite clays from Kamenets-Podolsk and Uzhgorod. To compare the properties of montmorillonite and kaolinite clays, Dubrovsky kaolin was studied.

Table 1 shows the chemical composition of the clays investigated.

TABLE 1

Chemical Composition of Clays in %

Clays	SiO_2	TiO_2	Al_2O_3	$Fe_2O_3 + FeO$	MgO	CaO	$Na_2O + K_2O$	SO_3	Hygroscopic H_2O	Loss on ignition	Total	$SiO_2 : Al_2O_3$
Askangel	57.00	0.32	19.99	2.79	2.13	1.26	2.59	0.89	8.52	5.16	100.65	5.0
Gumbrin	54.90	0.23	13.23	3.99	3.62	2.10	0.76	not found	15.36	6.36	100.54	7.0
Kamenets-Podolsk	50.96	0.15	16.76	1.90	4.34	2.66	0.52	0.58	14.90	7.94	100.44	5.2
Uzhgorod	51.30	0.84	23.38	5.58	1.30	0.56	0.70	0.20	7.26	9.24	100.36	3.9
Dubrovsky kaolin	46.54	0.15	35.86	1.19	0.86	0.56	1.54	0.30	0.90	12.62	100.52	2.2

Note. Manganese was found only in askangel, 0.18% (as MnO); phosphorus only in gumbrin, 0.50% (as P_2O_5); potassium was determined in askangel (0.92% K_2O) and Dubrovsky kaolin (0.73% K_2O).

The mineralogical composition of the clays was determined by the following methods: thermal, optical, and by dyeing with basic organic dyestuffs according to the technique developed by N. E. Vedeneeva.

Figure 1 shows thermograms of the clays, and Table 2 shows the endo- and exothermic breaks, determined from the heating curves, which characterize the mineral groups.

The optical method was used to determine the optical constants of the minerals, their approximate quantitative ratios, and microstructure. The refractive indexes were determined by the film method, with films prepared from the finest suspensions of the clays.

TABLE 2

Endo- and Exothermic Breaks on the Heating Curves of the Clays

Clays	Endothermic breaks, °C				Exothermic break, °C	Mineralogical composition
	1st	2nd	3rd	4th		
Gumbrin	130	660	850	None	None	Montmorillonite
Kamenets-Podolsk	170	700	860	None	None	Montmorillonite
Askangel	130	610	830	920	960	Montmorillonite
Uzhgorod	120	560	720	860	None	Beidellite
Dubrovsky kaolin	None	580	—	—	1000	Kaolinite

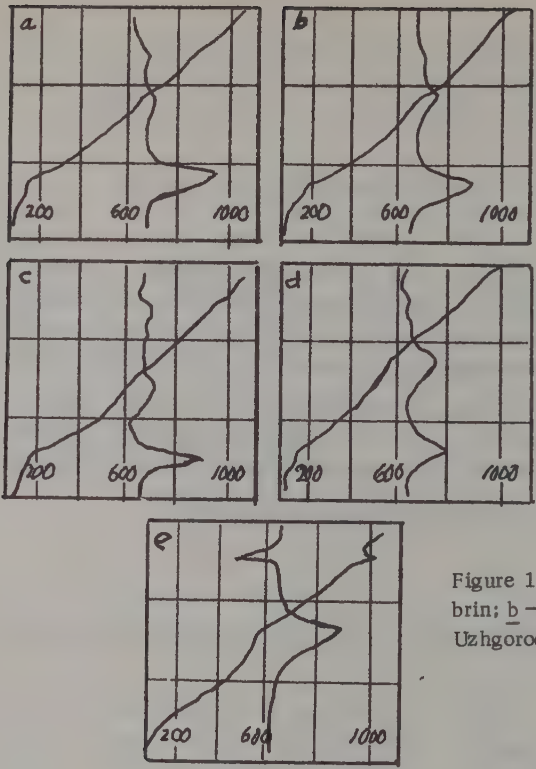

Figure 1. Thermograms for the clays: a — gumbrin; b — Kamenets-Podolsk; c — askangel; d — Uzhgorod; e — Dubrovsky kaolin.

The following mineralogical composition was established by these three methods:

1. Gumbrin contains 99% montmorillonite, individual grains of plagioclase.

2. Kamenets-Podolsk clay contains 99% montmorillonite, 0.5 — 1% plagioclase (or quartz), and individual grains of carbonates.

3. Askangel contains 75-80% montmorillonite, about 10% kaolinite, about 9-10% biotite and hydrobiotite, 3-4% plagioclases, individual grains of volcanic glass.

4. Uzhgorod clay contains 95% beidellite with an admixture of montmorillonite, 4.5% quartz, individual scales of hydromica.

5. Dubrovsky kaolin contains 75% kaolinite, 20-23% hydromica, 1-1.5% quartz, individual grains of carbonates.

Cation exchange capacity. The cation exchange capacity was determined according to Gedroits [1]. The results are shown in Table 3.

TABLE 3

Cation Exchange Capacity of Clays in mg-equiv./100 g

Clays	Sorption capacity	Composition of exchange cations		
		Ca^{2+}	Mg^{2+}	Na^{+}
Gumbrin	102.0	77.6	21.4	3.0
Kamenets-Podolsk	100.3	89.0	9.93	1.3
Askangel	80.4	30.9	8.70	40.8
Uzhgorod	40.5	29.7	7.91	2.9
Dubrovsky kaolin	9.4	7.7	0.37	1.3

Heats of wetting were determined with an adiabatic calorimeter by a method described previously by us [2]. The air-dry clay samples were sifted through a 0.1 mm mesh screen, dried at 110° for 10 hours, and sealed in ampoules. Other portions of the samples, before being sealed in ampoules, were held 8 hours in a vacuum thermostat at a minimum pressure of 10^{-4} mm Hg at 100°. The measurements were carried out at 20° in all cases. In addition, the effect of adsorbed cations on the heat of wetting of the clays was studied by replacing the Ca^{2+} by K, Na, and H ions. The results of the determinations are shown in Table 4.

TABLE 4

Heats of Wetting of Clays, in cal/g.

Clay	Natural clay	Natural, vacuum-treated	Ca-clay	H-clay	Na-clay	K-clay
Gumbrin	21.0	21.8	20.6	16.4	13.8	8.85
Kamenets-Podolsk	19.6	20.4	19.4	18.2	12.2	7.74
Askangel	11.0	11.7	18.2	15.0	9.96	5.13
Uzhgorod	11.0	11.7	9.76	8.79	6.76	6.24
Dubrovsky kaolin	0.95	1.56	1.05	0.94	0.89	0.87

Gumbrim and Kamenets-Podolsk clays have almost equal heats of wetting, which are high for clays. Ca-Askangel approaches them in value, but the heat of wetting of this clay in the natural state, when it is saturated mainly with Na^+, was about one-half that of the two preceding clays. Uzhgorod clay is far less hydrophilic. The coarsely dispersed Dubrovsky kaolin, consisting of immobile bunches of kaolinite particles, showed only a slight thermal effect on wetting. Adsorbed cations, as Table 4 shows, affect the values of the thermal effects of wetting of clays. As in the case of kaolins and kaolinite clays (see [4]) it is possible to establish, for bentonites, the following cation series in order of their effect on the integral heat of wetting:

$$Ca^{2+} > H^+ > Na^+ > K^+$$

Removal of gases from the clays in the vacuum thermostat produced an average increase of 0.75 cal/g in the heats of wetting.

It is known that the heat of wetting, due in the main to a decrease of surface energy, depends under otherwise equal conditions on the specific surface of the solid phase. Therefore, with a knowledge of the heat of wetting, it is possible to calculate the specific surface S_0 of one gram of clay from the Formula:

$$S_0 = \frac{Q}{q}\ \text{cm}^2$$

where Q is the heat of wetting in erg/g, q is the total surface energy of water, equal to 116 erg/cm^2 at 20°. The values of the effective specific surface of the clays calculated with the use of this formula are shown in Table 5.

TABLE 5

Effective Specific Surface and Amount of Bound Water

Clays	S_0 in cm^2/g	A in %	Maximum hygroscopic moisture determined gravimetrically, %
Gumbrin	787	21.7	19.0
Kamenets-Podolsk	735	20.3	19.2
Askangel	424	11.6	9.97
Uzhgorod	422	11.6	9.23
Dubrovsky kaolin	38.2	1.55	1.10

The high values of the specific surface of gumbrin and Kamenets-Podolsk clay are evidence of their high degree of dispersion.

To determine the amount of adsorbed water, the clays previously dried at 110° were placed in desiccators in open packets over a saturated solution of calcium nitrate, with considerable excess of solid phase. In these conditions the relative humidity of the air was 55% at 20°. After equilibrium was reached, the moisture content of the clays was determined by the usual gravimetric method.

The results of these experiments were compared with the amounts of bound water (A), calculated from the Formula

$$A = \frac{Q\ \text{erg}\ 2.76 \cdot 10^{-8} \cdot 100}{q}$$

It was assumed in the calculation that the clay particles are coated with a monomolecular layer of bound water, the thickness of which, from the hydrogen bond, is $2.76 \cdot 10^{-8}$ cm. The calculated values of A are shown in Table 5.

The relatively good agreement between the values for bound water found by the gravimetric method and those calculated from the heats of wetting of bentonites, as was also observed previously for kaolinite clays [3], indicates the reliability and validity of the latter method, and its applicability to the quantitative characterization of the hydrophilic properties of clays.

As Table 5 shows, the amount of bound water depends directly on the specific surface and the heat of wetting of the clays, which places gumbrin and Kamenets-Podolsk bentonite among the most hydrophilic bentonite clays of the Soviet Union.

Structure and sorptional properties of the clays.[*] The porosity and the specific surface characterize the structure of an adsorbent. To determine the volume of the pores according to their size we used the adsorptional-structural method developed by Dubinin and Kiselev [6, 7].

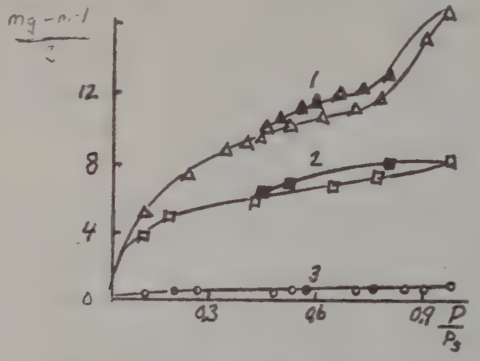

Figure 2. Isotherms for the sorption and desorption of water vapor (1), methyl alcohol (2), and heptane (3) on Kamenets-Podolsk clay.

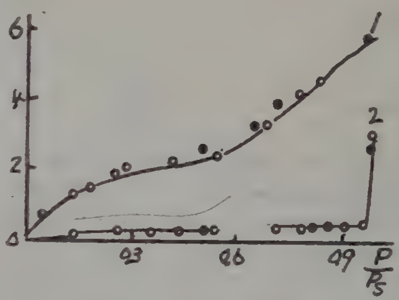

Figure 3. Sorption isotherms for methyl alcohol on Askangel (1) and Dubrovsky kaolin (2).

The sorption isotherms for vapors of water, methyl alcohol, and benzene were determined in a vacuum apparatus with a spring quartz balance constructed by K. V. Chmutov. The total porosity of the samples was determined from the values of apparent and true density, and the maximum sorptional capacity was determined with the use of vapors of benzene, water, and methyl alcohol. The structural-sorptional characteristics of the clays are shown in Table 6, and Figures 2 and 3 show the sorption isotherms.

TABLE 6

Structural-Sorptional Characteristics of Clays

Clays	Density g/cm^3		Total pore volume, cm^3/g	Vapor adsorbed, in % of saturation			Volume of adsorbed vapor in the liquid state when $p/p_s = 1$		
	Apparent	True		C_6H_6	H_2O	CH_3OH	C_6H_6	H_2O	CH_3OH
Kamenets-Podolsk	1.92	2.50	0.12	19.8	28.5	25.0	0.22	0.29	0.32
Askangel	1.95	2.60	0.11	9.9	—	16.4	0.11	–	0.21
Dubrovsky kaolin	1.11	2.50	0.50	12.9	—	3.0	0.15	–	–

The adsorption of methyl alcohol vapor on askangel and Dubrovsky kaolin is low, and reaches only 0.01-0.08 cm^3/g. The sorption isotherms for Kamenets-Podolsk bentonite are of a different nature; the adsorption ceases at relatively low values of p/p_s. The sorption isotherms show a hysteresis loop, and therefore, it may be supposed that capillary condensation commences during the adsorption of vapors under appreciable pressures.

Activation of Kamenets-Podolsk bentonite (Figure 4) by hydrochloric acid resulted in an increase of the total pore volume and sorptional capacity. Evidently, the chemical activation of clay is associated with ion exchange. This question requires further study.

Sorption on bentonite and askangel is a characteristic example of cases in which the gel skeleton is "non-rigid", and the structure of the adsorbent is changed during the sorption process itself. The volume of vapors adsorbed by these materials (Table 6) is greater than the total pore volume. Here, in addition to true adsorption, penetration of the sorbed substance into the clay skeleton takes place, and the degree of "non-rigidity" differs in relation to the sorption of different substances. The volume of the sorbed substances is greater for the polar molecules of water and methyl alcohol, than the volume of sorbed benzene.

It is curious that a stable reversible curve could be obtained only after the bentonite sample was held for a long time in a vacuum. This is due to the fact that, in addition to physical adsorption, some other more complex processes take place when the molecules of the sorbed substances are taken up.

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[*] This section of the work was carried jointly with I. E. Neimark and I. B. Slynyakova [5].

Electron microscope studies of bentonite clays showed that montorillonite particles are composed of scaly aggregates which are capable of moving apart during sorption of vapors, so forming additional surfaces between the plates. Hendricks [8] showed that organic nonpolar molecules are arranged on a surface in a layer of minimum thickness. This apparently accounts for the fact that the same adsorbent contained less adsorbed benzene than adsorbed methyl alcohol and water.

Analysis of the sorption isotherms for water and methyl alcohol vapors on Kamenets-Podolsk bentonite, and comparison of these with the isotherms for artificial adsorbents [9] shows that the bentonite studied is a good fine-pored adsorbent and may be used even without supplementary activation as a drying agent for gases and for adsorption of vapors at low concentrations.

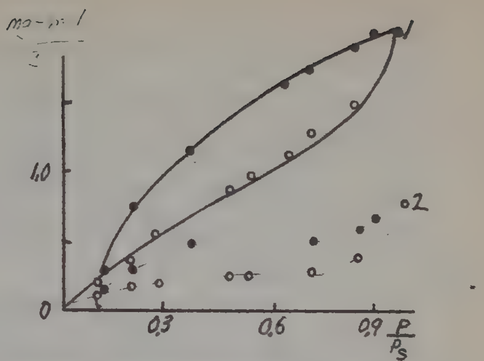

Figure 4. Sorption isotherms for heptane on activated (1) and nonactivated (2) Kamenets-Podolsk clay.

TABLE 7

Sorptional Properties of Ca, H, and K-Bentonites

Clay	Benzene		Methyl alcohol		Water	
	% sorption	Volume of sorbed material in cm^3/g	% sorption	Volume of sorbed material in cm^3/g	% sorption	Volume of sorbed material in cm^3/g
Ca-bentonite	19.8	0.22	25.0	0.32	28.5	0.29
H-bentonite	15.4	0.17	24.2	0.31	28.2	0.29
K-bentonite	12.7	0.14	17.0	0.22	21.6	0.22

Comparison of the adsorptional properties of Kamenets-Podolsk bentonite with the properties of natural adsorbents from the Far East and of other clays of the USSR [10] shows that Kamenets-Podolsk bentonite differs advantageously by a good sorption of vapors at relatively low pressures, and by a relatively large specific surface, which is a valuable property in an adsorbent.

The sorptional capacity of clays depends on the nature of the sorbed cation, as was confirmed in the case of Kamenets-Podolsk bentonite (Table 7).

SUMMARY

1. Determinations of the heats of wetting and moisture contents, and calculations of bound water and specific surface, were made for the clays studied. The most hydrophilic were gumbrin and Kamenets-Podolsk bentonite, and askangel and Uzhgorod beidellite were less hydrophilic. The maximum hygroscopic moisture content of the clays largely agrees with the amount of adsorptionally bound water calculated from heats of wetting.

2. The hydrophily of bentonites increases with increase of the molecular ratio $\frac{SiO_2}{Al_2O_3}$ in the chemical composition of the clay mineral, and with increase of the montmorillonite content in the clay.

3. It is shown that the hydrophilic and adsorptional properties of clays are affected by the value of the total exchange capacity and the nature of the adsorbed cations. The latter form the following series in order of their effect:

$$Ca^{2+} > H^+ > Na^+ > K^+$$

4. A study was made of the sorption and desorption isotherms for vapors of water, methyl alcohol, and benzene on specimens of Kamenets-Podolsk bentonite, askangel, and Dubrovsky kaolin. It was established that Kamenets-Podolsk bentonite has high sorptional power, close to that of artificial adsorbents.

5. A relationship between the hydrophily and the sorptional properties of bentonite clays is shown. The chemical and mineralogical composition, cation exchange capacity, and structure of the clays studied was established.

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DETERMINATION OF THE RHEOLOGICAL PROPERTIES OF CLAY SUSPENSIONS IN CONDITIONS OF STEADY MOTION

B. S. Filatov

In a number of branches of technology the necessity has long existed for the determination of the rheological properties of viscoplastic and other non-Newtonian bodies in conditions of steady flow. This problem arises, for example, in calculations of the operation of bearings with greases, in hydraulic calculations of the circulation of clay suspensions in drilling, hydraulic transport of clay soils, mud, paper pulp and a number of other systems [1, 2, 3]. The number of investigations which are devoted to studies of rheological properties of non-Newtonian bodies in conditions of steady shear is limited. Many papers in the field of rheology are mainly devoted to studies of the rheological properties of anomalous systems in static conditions and in conditions of non-steady shear [4]. This leaves unclarified questions of the relationship between the static and dynamic properties of a number of industrially important substances with anomalous viscosity. Sometimes these properties are merely taken as identical [2].

We showed [5] that in technical calculations of the flow of clay suspensions in pipes, used as drilling muds in oil wells, it is possible to apply successfully the values of structural viscosity* η and the dynamic limiting shear stress τ_0 determined from relationships founded on the Shvedov-Bingham hypothesis [6]. In connection with this work, comparative measurements of these magnitudes were made by two different methods.

1. Use was made of the results of experiments with the hydraulic apparatus described previously [5]. In experiments with a structural regime of flow of the suspension in pipes, the values of the maximum gradient of shearing rate (at the tube walls) was calculated, for a parabolic distribution of velocities:

$$\left(\frac{dv}{dr}\right)_{max} = \frac{4V}{R} = \frac{4Q}{\pi R^3} \tag{1}$$

and the maximum shear stress in the suspension (at the tube walls)

$$\tau_{max} = \frac{PR}{2L}, \tag{2}$$

where V is the average volume rate of flow of the suspension in the pipe in cm/sec; Q is the rate of volume flow of the liquid in cm^3/sec; R is the inner diameter of the pipe in cm; P is the pressure drop in the region of the pipe in question, in dynes/cm^2; L is the length of the section of the pipe in cm.

These values were plotted in Figure 1; the straight lines of Figure 1 are a graphical representation of the Buckingham equation [1, 2] without the last term:

$$\tau_{max} = \left(\frac{dv}{dr}\right)_{max} \eta + \frac{4}{3}\tau_0. \tag{3}$$

The experimental points for each series of experiments fit well on a straight line, which confirms the validity of the Shvedov-Bingham law for steady flow of clay suspensions, and, in particular, the applicability of the Buckingham equation to the flow of such suspensions in pipes. Deviations from a straight line, which should be found with small volume flow rates of liquid as the result of the influence of the neglected last term in the Buckingham equation, which allows for the existence of an undeformable core in the stream, are found only for very thick clay suspensions (lines 2 and 4 in Figure 1). For less concentrated suspensions such deviations are not found

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* This value is termed plastic viscosity in the papers of M. P. Volarovich.

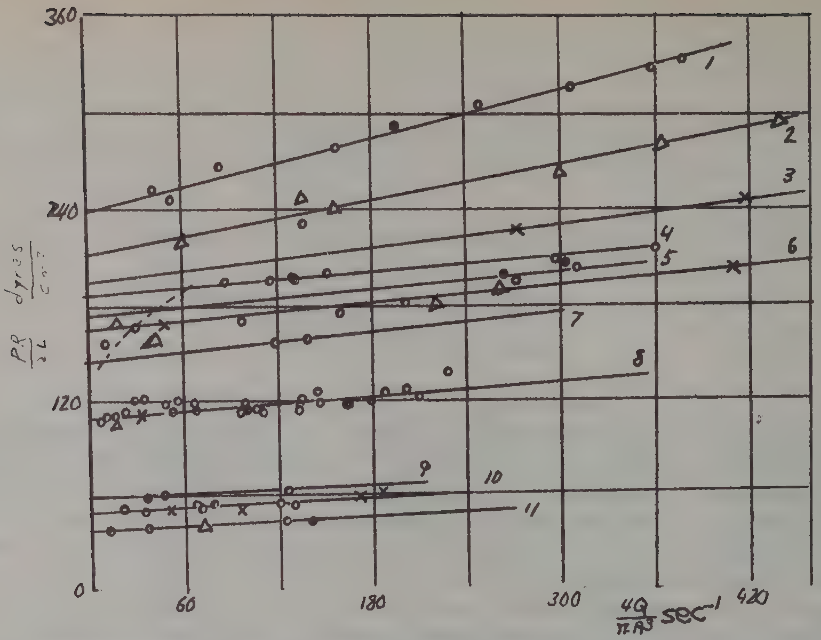

Fig. 1. Determination of structural viscosity and dynamic resistance to shear, from results of flow measurements in pipes (for Nos. of Curves, see Table 1): o) D = 6.32 cm; Δ) 5.30 cm; ×) 4.00 cm.

up to values

$$\left(\frac{dv}{dr}\right)_{max} = 20 \text{ sec.}^{-1}$$

The position of the straight lines in Figure 1 was found by the method of least squares. Points obtained for small liquid volumes which clearly deviated downward of a linear relationship, and also points which corresponded to the beginning of turbulence and deviated upward were neglected.

The value of the structural viscosity η was determined as the tangent of the angle of inclination of the straight lines to the abscissa axis:

$$\eta = \frac{\Delta\tau_{max}}{\Delta\left(\frac{dv}{dr}\right)_{max}}, \tag{4}$$

and the value of the dynamic limiting shear stress τ_0 as 3/4 of the value of τ_{max}, determined by the intersection of the straight line $\tau_{max} = f\left(\frac{dv}{dr}\right)_{max}$ with the ordinate axis.

The properties of the clay suspensions studied are shown in Table 1.

The experimental series 1-3 was carried out with suspensions of the relatively weakly colloidal clay from the Kudinovo station of the Moscow-Kursk railroad, and the experimental series 4-11 with suspensions of the highly colloidal bentonite clay from Askangel (Georgia). Suspensions of Askangel clay show considerable variations of η and τ_0 for almost the same density γ. This is explained by differences in the degree of dispersion and, consequently, in the degree of hydration of the clay particles. The suspensions in the series 9-11, which had lower values of η and τ_0 than the suspensions of series 8 with a higher density (1.045 and 1.042 g/cm^3 respectively) were investigated soon after preparation, while suspensions of series 8 were subjected to vigorous stirring in rapid centrifugal pumps for a long time before the tests.

In the series 6, 8, 10, and 11 the experiments were performed simultaneously in several pipes of different diameters. It was found that the values of η and τ_0 did not depend on the pipe diameter within the limits of

TABLE 1
Properties of the Clay Suspensions

Lines No. (Experimental series)	γ g/cm^3	τ_0 dynes/cm^2	η poises	Internal diameter of pipes, cm
1	1.230	180	0.255	6.72
2	1.208	160	0.190	5.30
3	1.205	145	0.125	4.00
4	1.047	140	0.100	6.72
5	1.047	132	0.100	6.72
6	1.047	121	0.100	6.72, 5.30 and 4.00
7	1.047	108	0.100	6.72
8	1.042	82	0.067	6.72, 5.30 and 4.00
9	1.045	45	0.04	6.72
10	1.045	39	0.04	6.72 and 4.00
11	1.045	30	0.04	6.72 and 5.30

measurement in our experiments.

2. Measurements of τ_0 and η were carried out in a rotational viscosimeter which was constructed by us jointly with S. Yu. Zhukhovitsky, and which is shown in Figure 2.

The base plate, stand, and suspension system with the stationary cylinder were taken from the standard SNS-1 apparatus for the determination of the static shear stress of clay suspensions [7]. To obtain different rates of rotation of the outer cylinder, the base plate of the apparatus was fitted with a laboratory synchronous motor, two-stage transmission, and a plate clutch. A revolution counter was attached to the lower end of the roller on the outer cylinder, to measure the rate of rotation. The clay suspensions were placed in the gap between interchangeable bronze rings with a smooth inner surface, inserted in the rotating outer cylinder, and the inner stationary cylinder, made from stainless steel and with longitudinal ridges on its peripheral surface to prevent slippage, and a cup-like depression in its lower face to prevent friction by forming an air cushion. The average radius of the inner cylinder was $R_{av} = 2.003$ cm, its length $\underline{l} = 6.00$ cm, the average width of the gap of the working space of the viscosimeter for ring $\underline{1}$ was 0.098 cm, and for ring $\underline{2}$, 0.192 cm. The inner cylinder was suspended from the stand by interchangeable steel threads, the elasticity of which was measured at intervals by the torsional vibration method.

Measurement technique. The clay suspension, usually taken from the hydraulic installation immediately after the conclusion of a series of experiments, was poured into the outer cylinder. The highest rate of rotation of the outer cylinder, equal to 4.5-5 revolutions per second, was established, and this rate was maintained until the torsion angle of the thread ceased to decrease. For Askangel clay suspensions this decrease of the torsion angle at a constant rate of rotation ceased at the end of 2-5 minutes, and for suspensions of Kudinovo clay, after 8-15 minutes. The seconds clock was then switched on, and the initial reading of the revolution counter was recorded simultaneously. After 40-60 seconds, a second reading was taken and the clock was switched off. In the interval between the counter readings, the angle of torsion of the suspension thread was measured and noted. The rate of rotation was then decreased without the rotation being stopped, and the next measurement was made. A total of 6 to 20 measurements were made in each experiment. The experimental data were evaluated with the usual formula [8], derived by integration of the Shvedov-Bingham equation for the case of rotation of two concentric cylinders:

$$M = \frac{4\pi R_i^2 R_{av}^2 l}{R_i^2 - R_{av}^2} \eta \left(\Omega + \frac{\tau_0}{\eta} \ln \frac{R_i}{R_{av}} \right), \qquad (5)$$

where $\underline{M}$ is the torsion moment of the viscosimeter suspension system, in dynes/cm; $\underline{R_i}$ is the inner radius of the bronze ring in the rotating cylinder, in cm; $\underline{\Omega}$ is the angular velocity of rotation of the outer cylinder in rad/sec.

The formula (5) is valid only if the shear is distributed through the whole mass of the suspension in the gap. In the gap dimensions between the inner and outer cylinders which were used in our experiments, this condition was observed for nearly all the experimental points.

The experimental data were recalculated in terms of the values: $2\pi \frac{\Delta n}{t}$ and

$$\frac{K\Delta\varphi (R_i^2 - R_{av}^2)}{4\pi R_i^2 R_{av}^2 \underline{l}} \qquad (6)$$

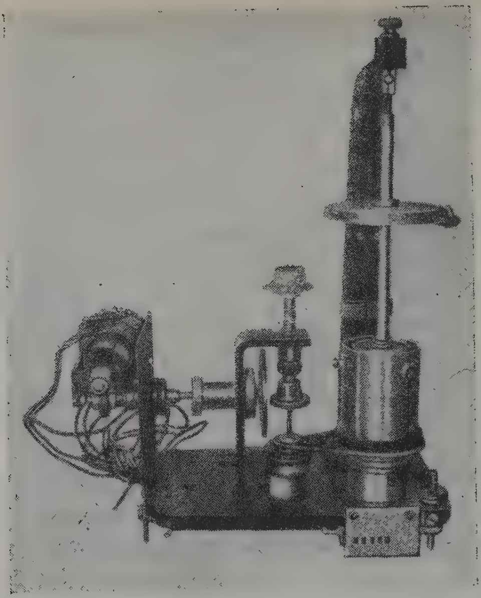

Fig. 2. Rotational viscosimeter (explanations in text).

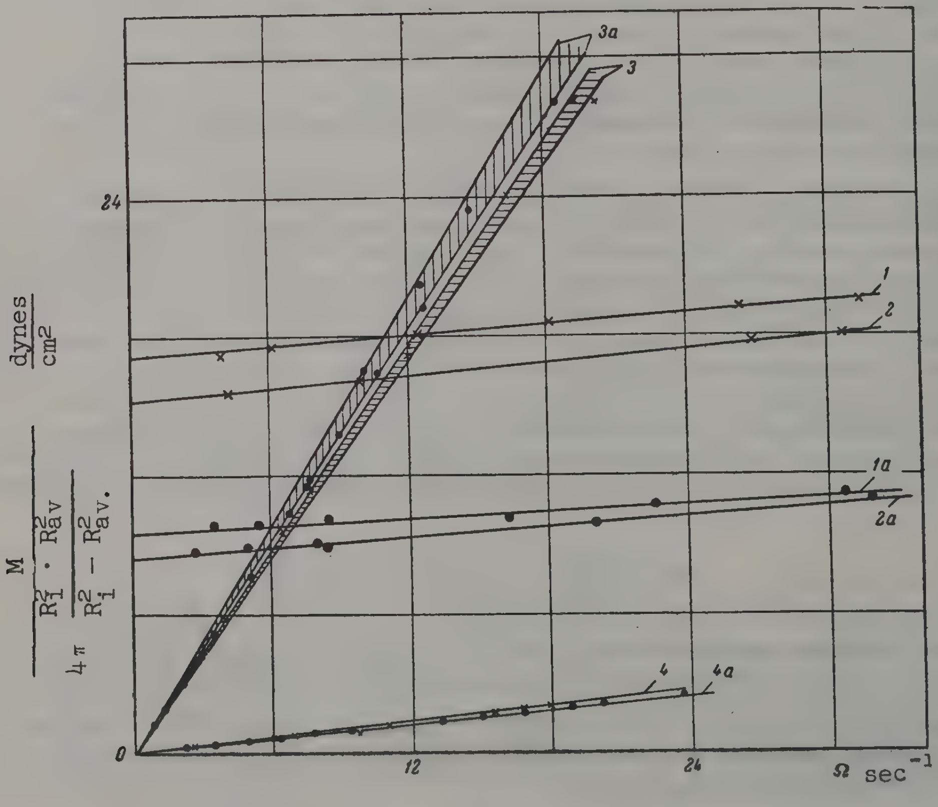

Fig. 3. Determination of the structural viscosity and dynamic shear stress with a rotational viscosimeter: 1 and 1a, 2 and 2a) see Table 2; 3) limits of the viscosity changes of the oil used for calibration in work with a gap of 0.192 cm; 3a) the same, for a gap of 0.098 cm; 4) viscosity of a mixture of glycerin and water in calibration with a gap of 0.192 cm; 4a) the same, for a gap of 0.098 cm.

where Δn is the difference between the counter readings in the time t of the experiment, $\Delta\varphi$ is the angle of torsion of the suspension system, K is the elasticity of the thread in dynes cm/ 1° ($K\Delta\varphi = M$). The experimental data were used to plot graphs in which values of Ω were taken along the abscissa axis, and values of the expression (6) along the ordinate axis.

To determine the structural viscosity from these graphs it is necessary to measure the tangent of the angle of inclination of the straight-line portion of the line, which expressed quantitatively the value of η. To find the dynamic limiting shear stress, it is necessary to divide the reading on the ordinate scale at the point where it cuts the straight-line portion of the line, by $\ln \frac{R_i}{R_{av}}$.

Figure 3 shows typical examples from a large number of measurements on Askangel clay suspensions. The results of calculation of η and τ_0 are shown in Table 2.

The results for suspensions of Kudinovo clay were not as definite. This is apparently explained by the presence in these fractions of a large content of coarsely dispersed fractions, which settle out in the working gap of the viscosimeter.

Figure 3 also shows results of the calibration of the rotational viscosimeter with standard liquids: mixtures of glycerin and water (viscosity 0.107 poise for measurements with a 0.098 cm gap, and 0.115 poise with a 0.192 cm gap), and oil. The viscosity of the oil changed during the calibration, because of temperature fluctuations, between 1.41 and 1.63 poises. The greatest deviations of the measured viscosities from the true values did not exceed 6% with a 0.098 cm gap, and 3% with a 0.192 cm gap.

TABLE 2

Comparison of Values of η and τ_0 Determined by Different Methods.

No. of lines of Fig. 3.	Gap in cm	Type of suspension	τ_0 dynes/cm^2		η poise	
			Pipes	Viscosimeter	Pipes	Viscosimeter
1	0.192	Suspension of Askangel clay, $\gamma = 1.047$ g/cm^3, experiment 18. VII, 1951	132	186.5	0.10	0.075
1a	0.098			199		0.05
2	0.192	Suspension of Askangel clay, $\gamma = 1.047$ g/cm^3, experiment 25, VII, 1951	121	166	0.10	0.098
2a	0.098			176.5		0.075

DISCUSSION

There are certain discrepancies between the results of measurements by the first and the second method, namely: measurements in the rotational viscosimeter give higher values for τ_0 than in pipes, and this difference increases with smaller gaps; the value of η follows an inverse relationship. Similar effects were observed by Zhigach and Zlotnik [9] for suspensions of Dzhebel bentonite clay, and by Green and Weltmann [10] for paint suspensions.

To explain the form of their viscosimetric curves, Green and Weltmann proposed a theory of the existence of two structures: a "flocculational" structure, which is destroyed in the initial stages of motion of the system, and a hypothetical "thixotropic" structure, which they assume to be capable of existence even at very high gradients of shear rate. Different shear rates correspond to different levels of destruction of the "thixotropic structure" which, together with orientation of free particles (those detached from the aggregates which survive at a given level) in the direction of the motion, determine the rheological properties of the system. Another attempt to explain the mechanism of phenomena which occur during flow of thixotropic disperse systems was made by Goodeeve and Whitfield [11], on the assumption that each shear rate corresponds to an equilibrium between the destruction and restoration of the thixotropic structure. Zhigach and Zlotnik [9] also consider that the continuous decrease of "effective viscosity" of the dzhebelite suspensions studied by them with increase of the shear rate gradient is explained by the existence of a "residual structure", similar in nature to the static thixotropic structure, which is gradually destroyed as the shear rate increases. In their view, complete destruction of this structure is to be expected at sufficiently high shear rate gradients, as shown by a constant value of the "effective viscosity":

Rabinerson [12] showed convincingly that it is not possible, on the basis of assumptions of a slow destruction of some rigid structure in a stream of a true viscous liquid, to explain the existence of forces of resistance to flow which are independent of the rate, in agreement with the Shvedov-Bingham hypothesis, and that a logical consequence of these assumptions is the interdependence of the shearing stress and the gradient of the rate of shear, proposed by Ostwald and De Waele [13]:

$$-\frac{dv}{dr} = K\tau^{n}, \tag{7}$$

where the coefficients K and n can vary during destruction of the structure. For clay suspensions, extensive experimental data support the validity of the Shvedov-Bingham hypothesis up to the commencement of turbulence. For example, Zlotnik [9] did not find constant values of the "effective viscosity" for 2.4% suspensions of dzhebelite up to 1000 $\sec^{-1}$ shear velocity gradients. In some of Shishchenko's experiments [2] the commencement of turbulence in the flow of clay suspensions in pipes of 3 mm diameter took place at a mean volume rate of flow equal to 3.30-3.40 m/sec. Up to these rates the flow followed the Shvedov-Bingham law, although the maximum shear rate gradient at the tube walls reached $10^4 \sec^{-1}$. In addition, the views in question cannot explain the opposing nature of the action of changes in the shear rate gradient on the structural viscosity and the dynamic shear stress.

To explain the plastic properties of certain colloidal systems, which are manifested in the presence of a component of the resistance forces which does not vary with the flow rate, it is necessary to assume either the existence of direct bonds between the particles of the solid phase through all the volume of the disperse system, or the existence of interacting fields of force near these particles. In the first case this constant component of the resistance to shear will be determined by the frictional forces between the solid particles, and in the second, by the interaction of the fields of force. The first factor plays the predominant part in disperse systems with high concentrations of the solid phase, of the order of 30% [14]. The second factor is apparently significant in those disperse systems in which dynamic resistance to shear appears even at low concentrations of the disperse phase, such as highly disperse bentonite clays. Houwink [15] indicates the great difference between ionogenic and noniogenic suspensions in the solid phase concentrations at which dynamic resistance to shear begins to appear. He attributes the existence of dynamic resistance to shear in ionogenic suspensions of low concentrations to the action of the field of force of the ionic double layer.

On the basis of the above, the following explanation may be put forward for the shape of the experimental viscosimetric curves for clay suspensions. In the initial stages of the motion the coagulational spatial structure is destroyed. This process is represented by the curved initial portion of the viscosimetric curve, which may be, with some degree of accuracy, described by Equation (7). As the rate of flow increases, the shear spreads across the stream; the remaining structural aggregates are destroyed, the flow becomes pseudolaminar [16] and finally laminar. This process corresponds to the straight portion of the viscosimetric curve, the continuation of which does not pass through the ordinate origin and which can no longer be represented by Equation (7).

Microcinematography of the laminar flow of disperse systems of anisodiametric particles in polarized light [16] and also direct observations under the ultramicroscope [17] show that the dispersed particles are oriented in the direction of flow and arrange themselves in layers. Between these layers are layers of the liquid phase, in which shear takes place. These observations are in good agreement with the fact, established by us [5], that turbulence is extinguished by particles of the solid phase in flow of clay suspensions; this fact, apparently, has a much more general significance [3, 18]. These effects are not in accordance with views founded on the theory of "early turbulence" of Ostwald [19], according to which the solid phase particles in suspensions in random motion act as propellers, produce numerous local eddies and cause early turbulence [20].

The relative displacement of layers of clay particles, surrounded by more or less powerful force fields of the ionic double layer, is accompanied by the formation of forces of resistance which do not depend on the shear rate. The magnitude of these forces is determined by factors other than the stability of the spatial coagulational structure, and it can be both less and greater than the latter. These forces appear only during motion; when the motion ceases, the layer structure is reformed into the normal spatial thixotropic structure.

The forces of resistance to shear, which depend on the rate, and which are characterized by the value of the structural viscosity, are determined by the true viscosity of the dispersion medium and by the interaction between the external diffusion regions of the hydration envelopes of the clay particles when layers of these particles are displaced. Evidently, the outer layers of these envelopes will become torn away at certain values of the shear rate gradient. At the same time, the outer layer of the ionic double layer, associated with the zeta-potential, should become detached from the clay particles. These processes should lead to an increase of the forces of resistance to shear, independent of the rate, first because of the exposure of firmer layers of the hydration envelopes, nearer to solids in properties, and second because of the intensification of the electric field round the clay particles. Transition of part of the bound dispersion medium into the free state should decrease the structural viscosity, which maintains its value when the shear rate is lowered in a definite time, as the processes of hydration are slow.

Thus, the views put forward provide an explanation of the experimental facts.

The maximum shear rate gradients at the tube walls at the commencement of turbulence did not exceed 400 $\sec^{-1}$ for the most concentrated suspensions, as Figure 1 shows, while the mean gradients across the tube were considerably less. On the other hand, in the viscosimeter preliminary stabilization of the suspensions took place when the shear rate gradient in the working volume was almost uniform, equal to 1000 $\sec^{-1}$ with ring 1 with $R_r = 2.100$ cm, and about 500 $\sec^{-1}$ with ring 2 with $R_r = 2.195$ cm.

These views are also confirmed by experimental data on the effect of temperature on the rheological properties of clay suspensions. It is known that the structural viscosity of clay suspensions decreases, and their dynamic resistance increases, with rise of temperature [21]. The explanation is that the diffusion processes, which become intensified with rise of temperature, act in the same direction as increase of the shear rate gradient.

SUMMARY

1. To explain the shape of the straight-line portion of the viscosimetric curve which is obtained for clay suspensions, and the dependence of the structural (plastic) viscosity η and the dynamic limiting shear stress τ_0 of these suspensions on the shear rate gradient, it is necessary to abandon concepts of so-called "thixotropic" or "residual" structures, etc., which are supposed to exist in steady flow of suspensions and which continue to be destroyed as the shear rate increases. These effects may be explained on the basis of the experimentally determined fact that the moving suspensions have a laminar structure, and by examination of the influence of the effect of the motion of the surrounding medium on the micelles.

2. The magnitude of the resistance to motion of clay suspensions in steady flow is determined by factors other than the stability of the coagulational, thixotropic structure, and it can be either less or greater than the latter. Viscosimetric methods based on measurements of rheological properties in static conditions or in conditions of nonsteady shear are inapplicable for the evaluation of these forces.

3. Both the viscous and the plastic forces of resistance to motion in established laminar flow of clay suspensions depend on the value of the maximum gradient of shear rate to which the system is subjected, and the duration of its action. The values of τ_0 measured for high gradients of shear rate may be considerably greater, and the values of η less than the values found for low gradients. These values remain constant when the motion continues with decreased shear rate gradients.

4. The construction of viscosimeters and the technique of measurement of structural viscosity and dynamic maximum shear stress for the technical calculation of motion of clay suspensions and other similar systems should ensure that the following requirements are satisfied:

a) The system initially studied should be subjected to uniform shear for the time necessary to stabilize the system at the shear rate gradient which corresponds to the effective value of this gradient in the equipment which is being designed;

b) Several pairs of results on shear rates and the corresponding forces of resistance to shear should be obtained by a progressive decrease of the shear rate without cessation of the motion.

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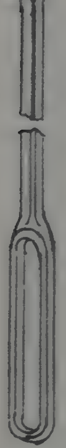
* See Consultants Bureau Translation, page 73

** See Consultants Bureau Translation, page 153

OSMOMETER FOR STUDY OF HIGH POLYMER SOLUTIONS

V. A. Vilensky

Many different osmometer constructions for the measurement of osmotic pressure of high polymer solutions have been described. The constructions described, however, have various defects. For example, questions of the nature of the membrane and of making the osmotic cell hermetically tight, are not yet solved. The attention of authors of the most recent designs [1, 2] has been directed to the question of sealing by mechanical means. It is, however, to be expected that the mechanical method cannot lead to reliable results, as the necessary tightness is not ensured by gripping the membrane between the surfaces of the rigid parts of the osmometer, which is the cause of the considerable number of unsuccessful experiments in such cases. This situation led to the development of the osmotic cell described below.



Osmometer for high polymer solutions.

Our osmotic cell is shown in the Figure; its construction is as follows: a thick-walled capillary with internal diameter of 0.5-0.7 mm is sealed to a section of tubing, sealed at one end, of 14-15 mm diameter, wall thickness ~ 1.5 mm, and length 6-7 mm. Two "windows" are ground away on the opposite sides of this tube along its whole length parallel to the axis of the cell. As the edges of the "windows" are covered with numerous minute cracks as a result of the grinding, the edges should be fused to strengthen them. The body of the osmotic cell is thus prepared.

The membrane is applied in two stages: first, by immersion into collodion solution (the lower end of the capillary being closed with a cotton wool plug), the surface of the body is coated with a layer of collodion, which is dried to a horny state. The collodion should also cover the capillary for a length of 7-8 cm. After drying, the collodion layer is cut along the inner edges of the "windows", and the collodion which covers the inner surface of the cell is removed together with the cotton wool plug. The body prepared in this manner is brought in contact with the surface of a collodion solution at the edges of the "windows", when the "windows" become closed collodion membranes, the edges of which are hermetically sealed to the collodion coating of the body. Membranes of varying permeability may be obtained with different times of drying (usually not longer than 15 minutes).

The tension which is set up when the membranes are dried is very convenient for subsequent work with the cells. However, these tensions may lead to breakage of the body if its walls are not thick enough or if the edges of the "windows" are not fused. The following collodion composition was generally used: 20 ml alcohol and 80 ml ether per 10 g nitrocellulose.

These osmotic cells are very convenient for work with aqueous solutions of high polymers. If the solution being studied swells or dissolves nitrocellulose, the osmotic cells should first be denitrated. This operation gives good results with the denitrating solution proposed by Zhukov, Poddubny, and Lebedev [2]. The only point of the denitrated osmotic cell at which the tightness may be impaired is at the end of the cellulose coating on the cell capillary. It is therefore advisable to cover this place with a small band of such a high polymer as is not affected by the system under investigation; for example, in alcohol-ether solutions it is very convenient to use a band formed by drying a solution of natural rubber.

No difficulties are found in filling (and therefore washing) the cells. A small piece of tubing 7-10 mm in diameter, drawn out into a long, thin capillary at one end, serves as a "funnel" which is used for filling the cell. It is very convenient to place a clamp with the "funnel" at the edge of the table. In this position, the flexible capillary of the "funnel" may be bent beyond the limits of the table; the cell may be easily fitted to the capillary of the "funnel" and then placed vertically on the table, directly under the "funnel".

Such cells may be used for equilibrium dialysis, with the difference, however, that the high polymer solution (because of the high weight concentration usual in dialysis) is more suitably placed not in the cell, but in an exterior vessel; the capillary of the cell can adequately be replaced by a thin-walled tube, when the cell can be filled and the tube sealed more rapidly.

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DISCUSSION

COMMENTS ON "ELECTROPHORESIS THROUGH COLLODION MEMBRANES"

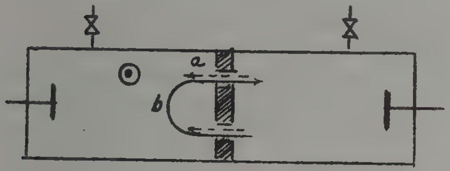
BY D. A. FRIDRIKHSBERG AND K. M. GUTMAN

[Colloid Journal, 15, 299, (1953)[*]]

Miroslav Toman

In their interesting paper the authors come to the conclusion, on the basis of experimental data, that "a countercurrent electroosmotic stream of liquid almost completely suppresses the passage of the dye through the membrane". Together with this explanation of the observed effects, another is possible, based on the unquestionably probable supposition that the diameter of the membrane pores is not uniform, but that their dimensions vary within some limits.

The corresponding scheme may be represented as follows (see Figure).



Scheme for the flow of a liquid through a membrane: a) direction of flow with taps open, and b) with taps closed.

Conditions do indeed exist in the pores for the establishment of electroosmotic flows, but only if the taps are open (in the Figure the direction of flow is shown by arrow a). However, if the system is in the closed state (with the taps closed), the electroosmotic pressures which arise in the pores will not have a decisive influence on the flow in the pores. The direction of the flow will be determined by the sign of the difference between the electroosmotic pressure which exists in the pore, and the additional pressure in one of the halves of the vessel. This means, however, that electroosmotic flow of the liquid will take place only in the small pores; in the larger pores (in which, according to the equation for electroosmotic pressure, the pressure set up will be inversely proportional to the square of the radius), the liquid will be forced out in the opposite direction (in the Figure the direction of the flow is shown by arrows b). Electroosmotic flow, which can only cause dilution of the dye, will be slower in a closed than in an open system; it is not necessary for its velocity to be zero, as is assumed by the authors. Dye solution is forced through the membrane in an amount which corresponds to the amount of liquid transferred by electroosmosis (the authors define this solution as being transferred electrophoretically).

I would like to refer to my paper (published in Chemicke Zvesti, 7, 1/2, 1953), in which the Zellner theory of anomalous osmosis is examined, and a new theory is put forward, both theories being based on the assumption of heterogeneous membrane pore dimensions. The further development of this theory, and evidence for its applicability to the laws of absorption of ions and water by plant cells, form the subject of a subsequent study, the results of which are not yet published.

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[*] See Consultants Bureau Translation, page 307.

REPLY TO COMMENTS BY MIROSLAV TOMAN

ON "ELECTROPHORESIS THROUGH COLLODION MEMBRANES"

BY D. A. FRIDRIKHSBERG AND K. M. GUTMAN

D. A. Fridrikhsberg and K. M. Gutman

The basic position established in our paper is that movement of the dye through the membrane is almost completely absent in an open system. Since there is no doubt that a potential gradient results in a directed motion of the dye, it was necessary to account for the retention of the dye, which was observed. Our proposed explanation, which described the experimental results quantitatively, is that of a "locking" action of a countercurrent electroosmotic stream in an open system. We could find no other explanation and cannot replace or supplement it by the explanation given in the comments (which essentially reduces to the existence of circulation of the streams), since no circulation can occur in an open system, as stated by the author of the comments himself (Figure 1, a). Therefore, the views developed in the comments do not affect the basic position of the "locking" action of the countercurrent stream in open system conditions.

In the case of a system with closed taps, M. Toman's comments are quite correct and relevant; calculation of the amount of dye which passes electrophoretically (or ionophoretically) through the membrane should be supplemented by the amount of dye "pressed" through as the result of circulation, in agreement with M. Toman's views. But, in this case also, (closed taps) the electrophoretic transfer not only does not vanish but it does not diminish. In fact, the supplementation of our views by the circulation and "pressing out" effects introduced by M. Toman, does not alter the electrophoretic calculation, as the motion of a particle or ion in an electric field is calculated relative to the liquid. Therefore, a correction for the velocity of the liquid itself must be introduced in the calculation of the linear velocity of the liquid relative to the membrane. However, summation for all the capillaries in closed circulation obviates this correction, as the aggregate velocity of the liquid for the entire membrane as a whole is zero.

Thus, the concept of the circulation of the solution should not alter the calculation of the amount of substance transferred by electrophoresis. To this amount it is necessary to add the amount pressed out as the result of electroosmotic circulation. Unfortunately, the calculation of this is difficult because it is impossible to assess the following factors exactly: 1) the fraction of the flow which appertains to the narrow pores, and, therefore, the amount of circulating solution (these values are complex functions of the pore distribution function); 2) the amount of the dye pressed out which enters adjoining narrow capillaries and returns to the original solution; 3) the effect of internal circulation in the capillaries (that is, movement of the liquid along the walls and opposite movement in the center portion) which occurs, for example, in a cell for microcataphoresis, and also of the extent to which the dye is transferred out of the capillaries in these conditions.

The calculations made in our study without account of the pressing-out effect, show that for methylene blue ($r = 171\ m\mu$) the calculated amounts are somewhat less than those found experimentally ($\underline{f} = 1.09$). This supports M. Toman's views and suggests that the "pressing-out" effect which he puts forward introduces in this case $\sim 10\%$ into the total transfer of dye through the membrane.

In conclusion, we wish to express our appreciation to Miroslav Toman for his great interest in our paper and for his valuable contribution, which makes it possible to broaden and deepen our concepts of the little-studied phenomenon of simultaneously occurring electrophoretic and electroosmotic processes in membranes.

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CURRENT EVENTS

THIRD ALL-UNION CONFERENCE ON COLLOID CHEMISTRY

G. I. Fuks and D. M. Sandomirsky

From December 21 to 24, 1953, the third All-Union Conference on Colloid Chemistry, convened by the Division of Chemical Sciences of the Academy of Sciences, USSR and the Division of Physico-Mathematical and Technical Sciences of the Academy of Sciences, Belorussian SSR, took place in Minsk.

The organization of All-Union Conferences on Colloid Chemistry in the capitals of the Republics of the Soviet Union has become a valuable tradition. The choice of Minsk as the venue of the next Conference is evidence of the development of chemical science in Belorussia. There is no doubt that the work of the Conference, in its turn, will have a favorable effect on the work on problems of colloid chemistry and its application by Belorussian scientists. The large number of delegates (over 150) indicates the considerable interest which the Conference aroused among wide circles of workers in the field of colloid chemistry and related sciences.

A total of 62 papers were presented at the Conference, including 10 at plenary sessions. The remaining papers were divided between three sections: aqueous suspensions and processes of structure formation, problems of stability and nonaqueous disperse systems, soaps and proteins. emulsions

It should be noted that the titles of the sections did not reflect quite accurately the subject matter of a number of papers presented to the sections. The papers presented at the Conference may be to some extent grouped in the following main subjects: structure of disperse systems, their rheological (physico-mechanical) properties, stability of colloidal solutions, suspensions, and emulsions, properties of thin layers at interphase boundaries, properties of high molecular compounds, and applications of colloid chemistry in the national economy.

In a short review, it is not possible to examine all the papers in detail. We are compelled to note only separate and the most important points in the papers, and in the case of a number of them, to confine ourselves to a mention of the subject or of the name of the author, in view of the proposed publication of the Conference Transactions.

The problem of the structure of disperse systems received extensive treatment. 17 papers dealt with this problem and related subjects. The papers dealt, in the main, with the following topics: 1) the mechanism of formation and the structure of colloidal particles; 2) mechanism of interaction of highly dispersed particles; 3) general questions of structure formation; 4) supermicellar structure and properties of technological materials. Individual papers dealt simultaneously with two or three of these groups of topics.

The mechanism of formation and the structure of colloidal particles received detailed experimental study, on the one hand, by Z. Ya. Berestneva and V. A. Kargin, and on the other, by A. V. Bromberg, M. V. Lukyanovich, V. V. Nemtsova, V. L. Radushkevich, and K. V. Chmutov, and was theoretically investigated by V. K. Semenchenko.

Z. Ya. Berestneva and V. A. Kargin reported the results of their electron microscope and electronographic investigation of the formation of colloidal particles of TiO_2, SiO_2, $Al(OH)_3$, V_2O_5 and gold. Previously to these studies it was considered that colloidal particles arise in the form of small crystals separated out of supersaturated solutions. Z. Ya. Berestneva and V. A. Kargin proved that in the initial state of formation of colloidal solutions relatively large spheroidal amorphous particles are formed which crystallize in the course of time and break up into large numbers of minute crystalline particles. The rate of this transformation depends on the nature of the system; in the case of colloidal gold the process is relatively rapid (about 5 minutes) while in the case of SiO_2 sols it lasts many months. It may be supposed on the basis of the extensive experimental material and the large number of systems studied by the authors that the formation of amorphous particles is a stage in the formation of all hydrophobic colloidal systems.

Considerable interest was aroused by the papers by A. V. Bromberg, V. M. Lukyanovich, and others, on investigations of the dimensions, form, and fine structure of colloidal particles (chiefly V_2O_5). These authors developed three methods for studying the growth of V_2O_5 rodlets, based on the use of the electron microscope. Elegant experiments disclosed certain peculiarities of fine structure of the nucleus of vanadium pentoxide micelles, and in particular it was shown that the ends of the rods have greater activity than the remaining surface. The mechanism of growth of V_2O_5 particles may be twofold: at high electrolyte concentrations oriented coagulation predominates, while in presence of small amounts of electrolyte the crystallization process prevails.

V. K. Semenchenko indicated the resemblance and differences between substances in the critical state and colloidal systems. Examination of peculiarities of the critical state or, more accurately, the critical region, led him to the conclusion that disperse systems of the usual type are near the boundaries of the critical region. Accordingly, the thermodynamics of disperse systems should essentially coincide with the thermodynamics of critical phenomena.

Questions of structure and dimensions of colloidal particles were also dealt with in certain other papers. N. F. Ermolenko and S. A. Levina studied the adsorptional activity of aluminum hydroxide in relation to the conditions and duration of its formation and the concentration of hydrogen ions in the dispersion medium. As a result of this work new factual data were obtained on adsorptional activity, and convincing proof was given of the amorphous structure of colloidal aluminum hydroxide at the instant of its formation, and of its subsequent conversion into the crystalline form. B. V. Erofeev reported on the relationship he found between the particle size distribution in disperse systems and the kinetics of their formation. The paper by M. P. Volarovich and N. V. Churaev was devoted to questions of study of particle structure and the degree of dispersion of a polydisperse system such as peat. The construction and theory was worked out for a new gravimetric sedimentometer for suspensions in which the difference between the densities of the disperse phase and the dispersion medium is small. With the use of this apparatus and of the electron microscope the authors succeeded for the first time in covering the entire curve for particle size distribution from hundredths of a micron to several millimeters.

The mechanism of the interaction of particles and macrosurfaces in liquids was the subject of the paper by B. V. Deryagin, N. I. Moskvitin, and M. F. Futran, and of the paper by G. I. Fuks. Part of the communication by N. A. Krotova also belonged to this group of papers.

B. V. Deryagin, N. I. Moskvitin, and M. F. Futran presented a paper with the title: "Energy of Adhesion of Bodies in Liquid Media and Its Kinetics as a Characteristic of the Solvation of Their Surfaces," The paper described a new variation of the crossed threads method for the measurement of the energy and kinetics of adhesion of solids, developed in the laboratory under the guidance of B. V. Deryagin. With the aid of this method, valuable data were obtained on the influence of various factors (temperature, concentration, and nature of the dissolved electrolytes and nonelectrolytes, etc.) on the energy of adhesion. These results give a deeper insight into the laws and mechanism of solvation of solid surfaces and the mechansim of protection and coagulation of colloidal systems. The paper produced a lively discussion, in which P. A. Rebinder, A. G. Pasynsky and others took part.

G. I. Fuks examined the general bases of study of interaction of solids in liquids by methods of adhesion and friction measurement, and described three new methods developed for such studies. It was shown that the distance between the particles is the principal factor which determines the nature of the forces of interaction, and data are presented which characterize the laws of kinetics of adhesion and detachment for different distances between the particles. Views were put forward concerning the nature of the nonchemical forces which act between highly dispersed particles.

N. A. Krotova reported on her studies on the nature of adhesion, the mechanism of separation of adhering bodies, and the effect of the rate on this process. The role of electrical forces in adhesion phenomena was examined in special detail, in the light of the theory developed jointly with B. V. Deryagin. N. A. Krotova (jointly with V. V. Karasev) discovered a new phenomenon of cold emission of electrons during the separation of high polymer films in a vacuum.

The central communication on questions of supermicellar structure formation in disperse systems was the paper by P. A. Rebinder on "Structure Formation and Peptization in Aqueous Suspensions". This paper combined a large group of studies carried out in the Institute of Physical Chemistry of the Academy of Sciences, USSR, and in the Department of Colloid Chemistry of the Lomonosov State University, Moscow, on supermicellar structure formation in disperse systems in relation to clarification of the mechanism of setting and hardening in concentrated aqueous suspensions of binding materials of various kinds (cements, gypsum, lime, clays). Studies of the role of peptization in thixotropic structure formation, and elucidation of the nature and laws of structure formation, led to new practical possibilities of control of setting and hardening of mineral binding agents by the addition of peptizing and stabilizing agents, which at the same time modify, by adsorption, the crystallization process of new formations.

In its theme and theoretical conception, P. A. Rebinder's paper was grouped with a number of communications devoted to applied aspects of supermicellar structure and to the elucidation of the mechanism of structure formation in technological materials. Such communications include the paper by V. V. Stolnikov on "Colloidochemical Factors of Structure formation in Concretes and Relation to the Problem of Impermeability and Durability of Concrete"; the papers by E. E. Segalova and O. I. Lukyanova on "The Influence of Added Organic Plasticizers and Gypsum on Structure Formation in Concentrated Cement Suspensions", the paper by B. Ya. Yampolsky and E. S. Soloveva on "Studies of the Kinetics of Hydrolysis and Hydration in Dilute Suspensions of Cement Minerals", and the paper by A. N. Adamovich on "The Effect of Surface-Active Additions on the Properties of Cement Suspensions and on the Conditions of Reinforcement of Sandy Soils". These papers developed further a new division of applied colloid chemistry—the colloid chemistry of mineral binding materials.

A very promising method of extensive action on structure formation in clays was developed by G. V. Vinogradov and co-workers; their paper gave a description of the principles of chemical transformation of hydrophilic aluminosilicates into hydrophobic, with the aim of producing highly structurized disperse systems in nonaqueous media. A new class of compounds was described, consisting of compounds of aluminosilicates with various organic substances. These systems retain the structure-forming capacity of the original clays together with the properties of the organic compounds concerned.

The problem of structure formation was dealt with in the papers by M. T. Polonsky, who studied the effect of temperature on bentonite clay suspensions, and F. D. Ovcharenko, who investigated the structural-mechanical properties of kaolin and montmorillonite clays. The first of these authors showed that the strength of the thixotropic structure of clays increases with rise of temperature, and the second showed a correlation between the amount of bound water, the heat of wetting, and the degree of dispersion of the clays on the one hand, and the limiting shear stress and plasticity numbers on the other.

On the basis of these results, F. D. Ovcharenko proposed a method of determination of plasticity of clays.

An interesting and peculiar form of structure formation in suspensions was reported by I. N. Putilova and L. G. Gindin; they studied the laws of orientation and aggregation of microscopic particles of metals, semiconductors (boron carbide, copper suboxide), and soaps, suspended in liquid dielectrics placed in a constant electrical field. The results obtained have provided additional information on the mechanism of structure formation of disperse systems; at the same time, the significance of this paper passes beyond the limits of colloid chemistry, as it discloses certain causes of penetration of technical dielectrics and the nature of operation of electrical devices with conductors in powder form.

In recent years, B. A. Dogadkin and his co-workers have made an extensive study of the structure and of the mechanical, dielectric, and other properties of rubbers filled with carbon black. These studies have added substantially to knowledge of supermicellar structures in relation to nonaqueous disperse systems, developed concepts of the nature of the bonds between filler particles in rubber, and explained the technical properties of the systems in question. The following three papers were presented on these subjects at the Conference : 1) B. A. Dogadkin and K. A. Pechkovskaya, "The Structure of Carbon Black Rubbers and Its Changes under the Influence of Deformation and Heat"; 2) B. A. Dogadkin and A. I. Lukomskaya, "Dielectric Properties of the Rubber-Carbon Black System and of Filled Carbon Black Vulcanizates", 3) M.M. Reznikovsky and B.A. Dogadkin, "Internal Friction and Mechanical Losses in Carbon Black Rubbers at Different Loading Conditions". In the first paper, it was shown that carbon black is distributed in the rubber in the form of chain-like aggregates. The structure of the system is characterized by the number of rubber-carbon and carbon-carbon bonds and the relative proportion of each of these types of bonds. Deformation and heat change both parameters of the structure; the latter depend also on the type of carbon black. The second paper presented the results of a study of the effect of temperature and frequency on the dielectric constant and the dielectric loss angle of filled and unfilled rubbers. The study disclosed a number of peculiarities of the fine structure of the systems studied. The paper by Reznikovsky and Dogadkin differs somewhat from the two previous studies; it is devoted to an investigation of the dynamic characteristics of carbon black rubbers. The authors discovered laws with the aid of which it is possible, as a first approximation, to make a qualitative analysis of mechanical losses in rubbers under different conditions of dynamic loading.

The problem of the structure of disperse systems is closely associated and in many cases bound up with the problem of the mechanical properties of these systems. Twelve papers were presented at the Conference on questions of the rehology of disperse systems. The paper by M. P. Volarovich and L. Ya. Ginsburg described investigations of the rheological properties of high polymer solutions, used as adhesives. A relationship was found for solutions of natural and synthetic rubbers between their limiting shear stress and the structure studied by X-ray methods, and the adhesive properties — film strength, etc.. New methods for studying structural-mechanical properties were described in the papers by N. V. Mikhailov, "Study of the kinetics of development of elastic and viscoplastic deformations in bitumens and cement pastes", by A. A. Konstantinov, V. V. Sinitsyn, and G. V. Vinogradov on "Investigation of the viscous properties of highly structurized disperse systems with an automatic viscosimeter", by V. P. Pavlov on "Study of the viscous properties of disperse systems with a twin rotational viscosimeter", and K. I. Klimov on "the measurement of the strength limits of greases with a K-2 capillary plastometer". N. V. Mikhailov and his co-workers developed, and applied to the study of elastico-viscoplastic properties of bitumen and cement pastes, a precision apparatus comprising an electrically operated plastometer, by means of which it is possible to record automatically the kinetics of development of shear deformation and the corresponding stresses by oscillography over short periods of time (hundredths and thousandths of one second). The new apparatus has wide application potentialities. V. P. Pavlov provided an ingenious solution for the difficult problem of excluding the end effect of the bottom of the cylinder in the rotational viscosimeter, and so extended the potentialities and accuracy of apparatus of this type. A. A. Konstantinov and his co-workers devised an interesting and relatively simple capillary apparatus for the study and automatic recording of the viscosity of greases and other viscoelastic bodies.

A. A. Trapeznikov and V. A. Fedotova reported the results of their experimental work on the relationship between the deformational strength and viscous properties of oleophilic gels and on the thixotropy of fluid colloidal systesm. I. A. Dumansky presented a paper entitled "The elastico-plastic properties of highly viscous liquids and structurized systems". The Shvedov apparatus was used to study glycerin and solutions of cellulose xanthate, rosin, and saccharose; important conclusions were reached concerning the structure of these liquids. E. E. Kalmykova presented a paper on "The study of the structural-mechanical properties of cement pastes in the setting process".

Different types of deformation of strongly structurized disperse systems (mainly compound lubricant greases) were examined in the papers by G. V. Vinogradov and his co-workers. The following three communications were presented on this subject: 1) G. V. Vinogradov and V. G. Lebedev, "Investigation of the elastico-plastic and viscous properties of disperse systems in conditions of homogeneous stress"; 2) L. A. Shklyar, N. V. Tyabin, E. P. Mosikhin, and G. V. Vinogradov, "Behavior of structurized disperse systems in the field of action of centrifugal forces"; 3) E. P. Mosikhin and G. V. Vinogradov, "Investigation of rheological properties of highly structurized disperse systems in conditions of uniaxial extension". These papers add to the available information on the mechanical properties of plastic disperse systems, and also are of considerable interest from the point of view of experimental technique. In particular, while a fairly considerable number of studies on the shear deformation of greases have been published, the study by Vinogradov and Mosikhin is one of the first on the extension deformation of these materials.

The wall slippage effect in the flow of greases and other strongly structurized disperse systems through tubes and capillaries has a practical and theoretical significance. This question was the subject of a paper by V. V. Sinitsyn, who studied the viscous properties and wall slip of a number of industrial greases.

N. V. Tyabin presented a communication on the application of the equation for a viscoplastic medium to the study of the rheological properties of disperse systems.

I. N. Vlodavets read a paper on "The viscosity of liquids containing suspended particles".

The paper by Z. N. Markina, K. A. Pospelova, and P. A. Rebinder on "The effect of colloidal solubility on the structural-mechanical properties of aqueous solutions of sodium oleate" also, in part, belonged to the section on rheology. This paper also dealt with the important question of the nature of soap solutions.

A small group of papers touching on various phenomena at the interphase boundary was presented at the Conference; these included the paper by A. V. Taubman and E. K. Venstrem on "Laws of the effect of solutions of surface-active substances on the deformation and mechanical destruction of solids"; by B. Ya. Teitelbaum on "The formation of disperse systems in the surface layers of solutions"; and by S. G. Mokrushin on "The spontaneous formation of thin layers on the surfaces of hydrophobic gels".

The interesting paper by Taubman and Venstrem showed convincingly that the effect whereby the deformation of metals is facilitated by surface-active substances, which was discovered and studied by P. A. Rebinder and his coworkers, is typically adsorptional and obeys a number of laws which are characteristic of adsorption on liquid separation boundaries (with corrections for the specific influence of the nature of the metal). In the study of the adsorptional effect of facilitation of dispersibility, a number of specific phenomena which intensify this effect were established.

In a survey of papers on questions of stability of disperse systems and the nature of stabilizing layers, a further decrease is observed in the number of papers in the classical aspects of this field, and an intensification of a physical and even a physico-mechanical trend of investigations, which was already noted in the review of the papers presented at the Second All-Union Conference on Colloid Chemistry *. At the Minsk Conference no experimental studies were presented on electrokinetic phenomena or on measurements of solvation by the established physico-chemical methods (questions of solvation were examined from a new viewpoint in the papers by B. V. Deryagin and by N. I. Moskviti.. and G. I. Fuks, cited above).

In the paper on "The present state of the theory of stability of lyophobic suspensions and sols" B. V. Deryagin reviewed the present state of the problem of stability of disperse systems, and summarized a large number of his studies in this field, based on considerations of Van der Waals and electrostatic forces of interaction between the particles of the disperse phase. As is known, Deryagin's work has led to a theoretical basis for, and a quantitative expression of, the rules of Schulze and Hardy, and of Eilers and Korff, and of the role of the activity coefficient of the coagulant ion, empirically established in a somewhat different form by Wo. Ostwald. Deductions from the theoretical concepts of Deryagin were confirmed by the experimental studies of Yu. M. Glazman and G. I. Fuks.

On the subject of the coagulation of sols and other disperse systems by electrolytes, the Conference received a paper by Yu. M. Glazman on "The nature of the habituation effect in the coagulation of hydrophobic sols by electrolytes", and by S. S. Voyutsky, R. M. Panich, and K. A. Kalyanova on "Overcharge of the surface of particles in rubber dispersions (latexes) stabilized by soaps". Yu. M. Glazman showed that negative habituation should be the general effect of the gradual addition of electrolytes to the sol. Various side effects often distort the picture. S. S. Voyutsky and his co-workers established that in definite conditions there is a possibility of overcharge in emulsions stabilized by substances which do not have the power of changing the sign of the charge on alteration of the reaction of the medium. Suggestions concerning the mechanism of such overcharge are put forward.

E. M. Natanson read a paper on the subject of "An adsorptional-conductimetric method for the study of peptization of gels".

The mechanism of stabilization of foams and emulsions formed the subject of papers by A. S. Titievskaya and B. V. Deryagin, "The mechanism of the kinetic stability of nonaqueous foams and emulsions" and "The splitting action of free liquid films and its role in the stability of aqueous foams". In the first of these, a new method was used for the investigation of the kinetics of destruction of free films of nonaqueous solutions, and the results subjected to theoretical analysis. In the second, studies of the splitting effect were developed further in relation to free films, and the role of this effect was shown in the stability of foams, and an explanation was given for the decrease of foam stability by electrolytes.

S. E. Kharin presented a paper on the kinetics of latent slow coagulation of emulsions; he put forward an equation for calculating the rate of this process.

Questions relating to high polymers occupied a relatively small position at the Conference (this is explained by the fact that special conferences on these questions are regularly organized); thirteen papers were devoted to these, which may be divided into two groups: the properties of high polymer substances (nine papers) which included two papers on the techniques of investigating solutions, and emulsion polymerization (four papers).

Of the papers on techniques, great interest was aroused by N. V. Tsvetkov's papers on his refined technique for the measurement of forward and rotational diffusion in very dilute (down to 0.01%) solutions of high polymers at low velocity gradients. The results of these measurements show that over a wide range of molecular weights macromolecules behave in solution as opaque spherical bundles. The calculated radii of the equivalent spheres for insoluble chain molecules correspond to values which follow from statistical theories.

The paper by A. P. Vishnyakov on "Electrophoretic determination of protein fractions on paper" was also devoted to questions of experimental technique.

Questions of the structure of proteins, and changes in them under the action of various factors, were dealt with in a number of papers.

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* D. M. Sandomirsky and G. I. Fuks, Colloid J., 12, 396 (1950).

Great attention was aroused by the paper of A. G. Pasynsky on "The stability and lability of protein substances", devoted to clarification of the causes of specific colloido-chemical and biological properties of proteins. The speaker showed that these properties are determined by the simultaneous existence of high stability of configuration of the basic protein molecules, and great lability in their intermolecular relationships. It was shown that the asymmetry of albumin and globulin molecules changes relatively little even in harsh conditions, while in the normal physiological conditions only slight deformation of the molecules is to be expected. The high lability of proteins is due to the diversity of the chemical reactions of the functional groups and to the ease with which the aggregational equilibrium is displaced.

N. F. Ermolenko and D. Z. Ginzburg studied changes in the asymmetry of the molecules of vegetable protein from the lupin under the action of such denaturing substances as urea solution, caustic soda, and certain detergents.

A. V. Dumansky and P. A. Demchenko presented a paper on "Heats of wetting and lyophily of sodium soaps" in which they presented results of a study of the energy of interaction of soaps with water and hydrocarbons. R. V. Voitsekhovsky gave the results of a study of bound water in cellulose suspensions.

Production of a globular structure from linear polymers was the subject of a paper by P. I. Zubov, Z. N. Zhurkina, and V. A. Kargin. Studies of the properties of gels, solution viscosities, and also electron microscope data, all show that coiling of the molecular chains of rubber to form globular structures takes place under the influence of a number of factors. In the case of natural rubber this occurs, for example, by the action of vulcanizing agents, while in synthetic rubbers this process is apparently associated with the presence of extraneous groups and nature of the polymerization itself.

R. E. Neiman and O. V. Neiman devoted their interesting paper to an examination of the nature of gelation of high polymer solutions as a critical phenomenon, in agreement with the theoretical concepts developed by V. K. Semenchenko. An experimental basis for this conception is the anomalous stepwise variation of the coefficient of thermal expansion of gels, with a maximum on the coefficient of expansion—temperature curve.

Gels of high polymeric compounds were the subject of papers by M. S. Ostrikov, S. I. Pakhomov, and N. M. Sinelnikov, "Forces which cause the shrinkage of gels on drying", and by V. P. Rudi and A. A. Morozov, "The interaction between agar-agar and alcohol". S. A. Glikman and L. A. Root dealt with the topical question of the nature of solvation of high polymers in solvent mixtures.

A separate group consisted of papers on problems of emulsion polymerization. A. I. Yurzhenko and V. P. Gusyakov reported on the application of light scattering to the determination of the degree of dispersion of synthetic latexes. By the use of this relatively simple method the authors showed that the degree of dispersion of butadiene, isoprene, and styrene latexes is determined to a considerable extent by the concentration of the emulsifiers used. As the latter increases, the degree of dispersion increases also. The results may be explained on the assumption that the emulsified micelles are the centers of formation of the polymer globules. From this viewpoint it is also possible to explain the effect of the nature of the emulsifier on the dimensions of the polymer particles.

N. P. Apukhtina reported the results of a study of the effect of the structure of emulsified molecules and neutral salts on the yield of polymer. She showed, working with pure substances, that the dependence of the yield on the emulsifier concentration is substantially determined by the number of substituents in the molecule of the surface-active agent.

The mechanism of emulsion polymerization, and in particular, the site of formation of the polymer molecules, was the subject of papers by A. P. Sheinker, and S. S. Medvedev, and by P. M. Khomikovsky and S. S. Medvedev; the first of these described the results of a study of the kinetics of polymerization of dienes in colloidal solutions of detergents (cetyl pyridinium bromide).

It was found that the polymerization proceeds at first in the emulsifier micelles, and when these are exhausted, in adsorptional layers on the globules, out of the monomer dissolved in these layers.

P. M. Khomikovsky and S. S. Medvedev studied the chemical reactions which take place in disperse systems in the polymerization process, and they showed that emulsion polymerization occurs either in the water, or in the micelles, depending on the solubility of the monomer and initiator. In the polymerization of styrene in aqueous solution of the emulsifier, the activation energy is lowered in comparison with polymerization in a homogeneous liquid phase. This lowering is associated with a decrease in the energy of activation of initiator decomposition. In the polymerization of methyl methacrylate no lowering of the activation energy is observed, but the rate of polymerization increases at the expense of a decrease in the termination constant.

A series of papers at the Conference were devoted to a variety of applications of colloid chemistry in different branches of the national economy. Applied questions were also dealt with in some of the papers cited above.

Great interest was aroused by the extensive paper, presented at a plenary session, by A. V. Dumansky on "Methods of combating the filtration of water in canals and reservoirs, based on the use of alkaline humates". The present significance of the studies is quite evident in relation to the wide development of hydrotechnical construction in the Soviet Union. A large number of scientists from the laboratory of colloid chemistry of the Institute of General and Inorganic Chemistry of the Academy of Sciences, Ukrainian SSR, took part in the work; their extensive results obtained in laboratory and field conditions showed that the treatment of soils with alkaline suspensions of peat and brown coal followed by densification results in a sharp decrease of water filtration. A number of theoretical views were put forward in the paper concerning the mechanism of the action between humates and soils and of the changes in the physico-chemical and structural-mechanical properties of the latter.

The application of colloid chemistry to soil science was the subject of the paper by I. N. Antipov-Karataev, N. I. Gorbunov, and V. V. Kellerman on "The colloido-chemical nature of soil aggregates (soil structure) and methods of their analysis". This was a compilation of results obtained during studies of the structure of a large number of soil samples, with the use of a method of colloido-chemical analysis developed by the authors. It was shown in the paper that in the structural aggregate of soil the mineral components are joined together by organic material in the soil, and the structure of the aggregate and the nature of the adhesion depends on the soil reaction.

The subject matter of the remaining papers in this group covered a wide range; it included the structure of silicate glasses in relation to their color (M. A. Bezborodov), dyestuffs (L. I. Belenky), casein (P. F. Dyachemko and I. N. Vlodavets), questions of cellulose and paper manufacture (V. P. Derevyagina and S. L. Talmud), bread baking (B. A. Nikolaev) and others.

In general, the papers presented at the Conference are evidence of the further development of colloid science in the Soviet Union in the $3^1/_2$ years since the previous Conference. Valuable contributions were made to the development of the structure of colloids, studies of their stability, the physics and chemistry of high polymers, and to many other branches of science. Intensive development of various new questions of applied colloid chemistry is in progress. The significance of quantitative investigations of disperse systems has increased. There is a larger number of studies utilizing modern precision techniques (electron microscopy, oscillography, electronics, etc.). The relation between general questions of colloid chemistry and its applications has become firmer. It is remarkable that a number of general laws of colloid chemistry were discovered during the solution of applied problems (see the papers by P. A. Rebinder, A. G. Pasynsky, B. A. Dogadkin, G. V. Vinogradov, S. S. Voyutsky, their co-workers, and others).

The Organizing Committee achieved a great task in preparing the Conference. It is particularly necessary to note the efforts of N. F. Ermolenko and his closest assistants, who carried out the organization in Minsk. At the same time, the organization of the Conference was not without faults. These were chiefly due to an overloaded program. Because of the shortage of time, several of the papers submitted were not heard, while the discussion on a number of papers did not develop sufficiently. It is also regrettable that the papers were not preprinted before the Conference; this would have facilitated discussion. The 15-minute rule for papers on unpublished work was in many cases quite inadequate.

The intensive development of colloid science demands more frequent conferences and also, together with these, wide discussions on separate problems (as is done, for example, in the case of high polymers). The necessity has long existed for special meetings with extensive discussions and publication of papers on supermicellar structure, problems of stability, and questions of rheology of disperse systems.

Despite the certain defects, the work of the Third Conference on Colloid Chemistry was very fruitful; undoubtedly it will play a significant part in the further development of the science of disperse systems.

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